

Final Report for Task 2.3

PIER Transportation Research Area – Alternative Fuel Research Roadmap

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Acronyms and Abbreviations

AD.....	Anaerobic Digestion
AFAVDC	Alternative Fuels & Advanced Vehicle Data Center
AFEX	Ammonia Fiber Explosion
ARB	Air Resources Board
ARP.....	Ammonia Recycle Percolation
ASTM	Association Society for Testing and Materials
B5, B20, B100.....	5, 20, 100 Percent of Biodiesel in conventional diesel
bdt	bone dry tons
bdmt	bone dry metric tons
bcf	billion cubic feet
BEV.....	battery electric vehicle
bu.....	bushel
BTL.....	Gasified Biomass to Liquid
BTU.....	British Thermal Unit
CA-GREET.....	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model, modified for use in California
CARB.....	California Air Resources Board
CaRFG	California Reformulated Gasoline
CBP	Consolidated Bioprocessing
CBP	Consolidated Bioprocessing
CEC.....	California Energy Commission
CE-CERT.....	College of Engineering-Center for Environmental Research and Technology (University of California, Riverside)
CCS.....	Carbon Capture and Storage
C&D.....	Construction and Demolition
CNG	Compressed Natural Gas Cellulosic-E85 Cellulosic Ethanol
Corn-E85.....	Corn Ethanol
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CRC.....	Coordinating Research Council
CRP	Conservation Reserve Program
CSP	Concentrated Solar Power
CTL.....	Gasified Coal To Liquid
DBD	Dielectric-Barrier Discharge
DDPSC.....	Donald Danforth Plant Science Center
DGS.....	Distillers Grain with Solubles
DME.....	Dimethyl Ether
DOE	Department of Energy
E85	85% Ethanol, 15% gasoline
EISA.....	Energy Independence and Security Act
EPA.....	Environmental Protection Agency
EU	European Union
FAME	Fatty Acid Methyl Ester
FCV.....	Fuel Cell Vehicle

FFV	Flexible Fuel Vehicle
F-T.....	Fischer-Tropsch
gCO ₂ e/MJ	grams of carbon dioxide equivalent per megajoule of fuel delivered to the vehicle
GGE	Gallon Gasoline Equivalent
GHG.....	Greenhouse Gas
GMO.....	Genetically Modified Organism
REET.....	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model
GTAP	Global Trade Analysis Project
GTL.....	Gas-To-Liquid or GTL From Natural Gas
ha.....	Hectare
HC.....	Hydrocarbon
HFCV	Hydrogen Fuel Cell Vehicles
HHV	Higher Heating Value
HICE	Hydrogen Internal Combustion Engine
HRSO.....	Heated Rapeseed Oil
ILUC	Indirect Land Use Change
km	Kilometer
LANL.....	Los Alamos National Laboratory
LCFS	Low Carbon Fuel Standard
LPG.....	Liquefied Petroleum Gas (mixture of $\geq 90\%$ propane and $\leq 10\%$ other gases)
LUC.....	Land Use Change
M85.....	85% methanol, 15% gasoline
mbdt	million bone dry tons
mbdmt.....	million bone dry metric tons
mgy	million gallons per year
MIT	Massachusetts Institute of Technology
MJ	Megajoule
MSW.....	Municipal Solid Waste
MTG.....	Methanol to Gasoline
NAABB.....	National Alliance for Advanced Biofuels and Bioproducts
NO _x	Nitrogen Oxides
NG.....	Natural Gas
NGV	Natural Gas Vehicle
NREL.....	National Renewable Research Laboratory
NPGA.....	National Propane Gas Association
NRC	National Research Council
NSCA.....	National Society for Clean Air
PHEV	Plug-in Hybrid Electric Vehicles
PIER-TRA.....	Public Interest Energy Research- Transportation Research Area
PM.....	Particulate Matter
PTL	Gasified Petroleum Coke To Liquid
PV	PhotoVoltaic
REG.....	Renewable Energy Group

R&D.....	Research & Development
RD&D.....	Research Development & Demonstration
RFA.....	Renewable Fuels Association
RFS.....	Renewable Fuel Standard
RME.....	Rapeseed Methyl Ester
RMO.....	Rapeseed Oil
SME.....	Soymethyl Ester
SSCF.....	Simultaneous Saccharification and Cofermentation
tcf.....	trillion cubic feet
THC.....	Total Hydrocarbons
t/ha.....	tons/hectare
UK.....	United Kingdom
UCR.....	University of California at Riverside
US.....	United States
USD.....	United States Dollars
USDA.....	United States Department of Agriculture
WWTP.....	Waste-Water Treatment Plants
WTW.....	Well to Wheel
XTL.....	Liquid Fuel Production From A Number Of Feedstocks
yr.....	year
ZEV.....	Zero Emission Vehicle

Executive Summary

A concerted effort is being made at a State and National level to increase the use of alternative fuels in transportation and other areas. The legislature in California passed AB1007 (Pavley 2005) that requires the California Air Resources Board (CARB) and the California Energy Commission (CEC) to develop a plan to increase alternative fuel use in California to reduce oil dependency and air pollution. The State Alternative Fuels plan, developed under Assembly Bill 1007 (Pavley 2005), presents strategies and actions needed to increase the use of alternative non-petroleum fuels (CEC/CARB 2007). This includes milestone goals for the years 2012, 2017, and 2022, with a longer term plan for a multi-fuel transportation fuel infrastructure in California by 2050. Other State initiatives include Assembly Bill AB 118 (Nunez 2007) to create an alternative fuel and vehicle technology program, AB32 (Nunez/Pavley 2006), the Global Warming Solutions Act, and the Low Carbon Fuel Standard (LCFS) under CARB to reduce the carbon intensity of fuels.

In pursuing such aggressive implementation goals for alternative transportation fuel use, it is important to understand what limitations there are to the expansion of alternative fuels use and the role research and development can play in facilitating this expansion. To effectively utilize research funds in this area, it is important to establish goals and identify areas where research funding will provide the most value. The Public Interest Energy Research-Transportation Research Area (PIER-TRA) of CEC contracted with CE-CERT to develop a roadmap to guide its research efforts into the near and medium term. As part of the roadmap development process, CE-CERT produced several Alternative Fuels Technology Snapshot white papers addressing the state of various alternative fuel technologies in the areas of resource cost and supply potential, fuel production, distribution and utilization roadblocks, gap analysis and technology assessment, and recommendations of fuel pathways. These white papers formed the building blocks for this roadmap.

A summary of the *Technology and Commercialization Gaps, Potential Research Areas for Funding, and Research Recommendations* follows:

General Factors or Considerations

Scope of Fuel and Fuel Technologies Reviewed

This roadmap is specific to the PIER Transportation Alternative Fuels Research Area. This research area covers alternative fuels that are combustion-based. Electric vehicle technologies and their associated energy sources are covered under another section within the PIER Transportation Group. As such, electric vehicles and their associated fuel/energy sources are not covered under the scope of this roadmap. Fuel cell technologies are touched on in this roadmap, however, as the fuels used to power fuel cells, such as hydrogen and methanol, can also be utilized in internal combustion engines.

Vehicle Technology

The makeup of the vehicle fleet is one of the most critical factors in evaluating what fuels/technologies will have the best chance of success in the future. It is likely that a predominant fraction of the in-use vehicle fleet from now through the 2020-2030 timeframe will

be a combination of conventional vehicles and hybrid electric vehicles (HEVs). More advanced technology vehicles, such as plug-in hybrid electric vehicles (PHEVs), battery electric vehicles (BEVs), and fuel cell vehicles (FCVs), will likely not begin to significantly penetrate the market for new vehicle sales until the 2020 or later timeframe. Even under the most aggressively optimistic scenarios for the penetration of advanced vehicle technologies, where they would represent 87% of the entire fleet by 2050, these advanced technologies are expected to represent at most 25% of the in-use fleet by 2030. Irregardless of how optimistic these estimates are on the development and implementation of advanced electric/battery/hydrogen technologies, it is evident that liquid fuels will remain the predominant fuels for at least the next 30 years. Thus, funding resources for this time period should be allocated towards technologies and fuels that will produce renewable liquid-based fuels with low carbon intensities that can be produced within the State. This would include ethanol, other alcohols such as methanol and butanol, renewable diesel, such as biodiesel, Fischer-Tropsch diesel, or hydrogenated renewable diesel, or synthetic gasoline. Fuels such as CNG, LPG, hydrogen, DME would all require the introduction of specialized vehicles and fueling infrastructure that will not likely be feasible over the next 10-15 years, with the possible exception of commercial fleets. Thus, our recommendation is that the development of these fuels not be ignored but, from a pragmatic point of view, have a lower priority for research funding in the near-term. It is also worth noting that advanced vehicle technologies, such as hybrid/electric drivetrains, may have synergies with the development of renewable fuels. While a discussion of such synergies is beyond the scope of this work, this may be a consideration in evaluation future research efforts in fuels development by PIER.

Feedstock Availability and Technology Scalability in Meeting Transportation Fuel Needs

One of the most important considerations in evaluating technologies/fuels is the ability to meet the actual needs in the transportation fuels market. It is important to recognize the State of California uses over 16 billion gallons of liquid transportation fuels a year. Thus, any viable mix of energy conservation, feedstock, fuel production, public transportation improvement must have the potential to meet this energy demand in the future. From the standpoint of fuel production technologies, it is also important that the technologies being supported can be scalable to meet these needs, or at least be legitimate part of a portfolio of technologies that could meet these needs.

The availability of sufficient feedstocks in California will be another important driving factor in evaluating the technologies/fuels that will have the highest probability of success and meeting the fuel volume needs. From the results of previous studies, the distribution of potential feedstocks within the State will likely be regionally dependent. Forestry residues will likely be the predominant source in northern California. Agriculture biomass will be more prominent in the central part of the State. In urban areas and in the southern California area, municipal solid waste will likely be the most readily available feedstock source. Other feedstock sources such as algae or drought-tolerant energy crops may have a broader distribution within various parts of the state. In addition to the broader regional questions with respect to feedstock, it is also important to understand the concentration of feedstock that might be available within a reasonable transport distance to a production facility. While regional studies of potential feedstocks within California have been performed, there have been few/no studies of the optimal locations for facilities that would provide the greatest concentration of feedstock within a reasonable transportation distance. The local potential for various biomass feedstocks will be a

critical factor in determining if production facilities can be cost effective at various locations. Given the critical nature of this question, a study to characterize the local potential of various biomass feedstocks should be one of the highest research priorities, since this information will be central to determining what production technologies would be viable.

Environmental Issues

Environmental issues, such as greenhouse gas reductions and improvements in air quality, are some of the most important driving factors for the development of alternative fuels. Since environmental factors are critical to the promotion of alternative fuels, it is important to evaluate the environmental benefits/liabilities of various alternative fuels as they continue to be developed.

Some important methodologies in evaluating environmental impacts of various fuels are well-to-wheel and biomass production-to-wheel models. Although such models are being developed, their results are very dependent on the inputs. As such, these models should be reviewed by an independent body, their inputs scrutinized, and their outputs should be verified by experimental measurements. One of the most critical considerations in the development of well-to-wheel models was the impact of indirect land use changes, which occur when non-agricultural land is converted to agricultural uses in response to increased demand for biofuels. Although it is generally considered that indirect land use change is an important factor in evaluating fuels, there are still many uncertainties in how these estimates developed. It is also worth noting that CARB has not done well-to-wheel evaluations for thermochemical processes to date. The allocation of some PIER funds towards such analyses could be beneficial in determining how PIER funds should be distributed between thermochemical and biochemical processes. In California, all new fuels being brought into the marketplace must also undergo a comprehensive multimedia evaluation of any potential significant adverse impacts the fuel may have on public health or the environment, including air, water, or soil, that may result from the production, use, or disposal. This process is extensive and costly and could impact the ability to implement new fuels. While worth mentioning, the funding of such multimedia evaluations is beyond the scope of PIER's efforts, since fuels undergoing multimedia evaluation are typically relatively near the point of commercialization.

Developing Biorefineries that can Process Feedstocks in a Comprehensive Way

In developing a long term future for fuel production, it is important to develop facilities that will process the feedstock in a comprehensive way, i.e., convert the maximum amount of feedstock to viable products; produce the minimum amount of waste and the minimum amount of pollution. In this way, such fuel production facilities would be comprehensive biorefineries. This would include the processing of residual components to produce heat or energy that will meet a portion of the overall system requirements. The viability of such facilities could be evaluated with comprehensive process economic models.

Ethanol and Biobutanol from Corn and Sugarcane

Ethanol from corn is the most widely used alternative fuel in the US. Ethanol production is predominantly from starch- or sugar-based feedstocks such as corn (starch-based) in the US or sugarcane (sugar-based) in Brazil. The main limitations for this technology are the availability of feedstocks and regulatory limits on the amount of ethanol that can be used in gasoline.

Biobutanol has not been commercialized as yet, but is included in this section because it can be produced by modifications of the processes to produce ethanol and has some advantages over ethanol.

Status of Technology Development

- **Ethanol Production:** Ethanol production from corn and sugarcane technologies are mature enough for further expansion of the industry. The leading corn ethanol producers in the US are POET, LLC (formerly Broin), Archer Daniels Midland Co. (ADM), and Valero Renewable Fuels, LLC. The collective nameplate capacity of corn ethanol production facilities installed in the United States exceeded 13,000 MGY, with operating production greater than 11,800 MGY, as of January 2010. In Brazil, there has been a considerable expansion of sugar-based ethanol production, where there is abundant land for growing the crop. California has several ethanol plants in various stages of operation or planning, including facilities from AltraBiofuels Phoenix Bio Industries, Pacific Ethanol, Calgren Renewable Fuels, and California Ethanol + Power (sugar-based feedstocks), but the majority of conventional ethanol is produced in the Midwest.
- **Butanol Production:** Biobutanol production has not been commercialized, and it is currently more expensive to produce on a volumetric basis. One current method for biobutanol production involves fermenting corn starch using genetically modified yeasts. This basically involves modifying an ethanol production plant to make it a biobutanol production plant. While it is more expensive to produce butanol than ethanol on a volumetric basis, the costs of butanol may be slightly more favorable when the energy difference between ethanol and butanol is accounted for. If all ethanol plants were converted to biobutanol plants the levels of gasoline displacement would probably be similar to those that would be achieved with ethanol alone.

Technological and Commercialization Gaps

- **Feedstock Limitations:** Concern regarding the use of land and crops that could be used for human or animal food consumption will limit the extent to which starch or sugar-based ethanol production can expand. For 2009, for example, about one-third of the U.S. corn crop went to ethanol production, but this represented only 8% of the use of gasoline in the country on a volumetric basis, and an even lower fraction on a energy basis.
- **Vehicle Compatibility:** The use of ethanol in vehicles is limited by its compatibility with conventional vehicle technology. Currently, the use of ethanol in conventional gasoline vehicles is limited to 10-15% by regulatory limits and potential impacts on vehicle operation and durability. Although the blend limit for 2007 and newer model vehicles has recently been extended from 10 to 15% by the US EPA, with a similar extension for 2001 to 2006 under consideration, the continued restriction of the use of ethanol blends greater than 10% for vehicles older than 2001 will make it difficult to implement E15 on a retail level. Higher level blends, up to E85, can only be utilized in specially designed flexible fueled vehicles (FFVs), that still represent a relatively small fraction of the in-use vehicle population.
- **Production Maturity:** Since ethanol production from starch- or sugar-based feedstocks is a mature and commercial process, it is not expected that there are any significant advances in production that will dramatically improve the commercialization prospects of

conventional ethanol production. Additionally, while sugar-based ethanol can be successfully in Brazil, the limited acceptable crop acreage and higher sugar prices in the US make it more expensive to produce than corn-based ethanol in the US.

- **Utilization Issues:** While ethanol is already used extensively in blending with gasoline, there are a number of issues with the utilization of ethanol within the traditional petroleum infrastructure and with conventional gasoline vehicles. The number of fuel dispensers for higher blend levels, up to E85, is very limited, and it appears that there will also be a number of issues in developing a fuel dispenser infrastructure to accommodate any expansion of E15 use in newer technology vehicles. Another important limitation is that large scale ethanol delivery is impractical in the traditional pipeline system. Another limitation is the low energy density of ethanol compared to gasoline, and the corresponding reductions in fuel economy associated with this.

Potential Research Areas for Funding

- **Investigate most cost effective biobutanol production:** Biobutanol has some practical advantages over ethanol and it has been shown that current ethanol facilities can be modified to produce biobutanol. The advantages of butanol include its better compatibility with the petroleum infrastructure and vehicles and its higher volumetric energy content. Investing in determining the most cost effective method to produce biobutanol, whether by modifying existing ethanol facilities or building facilities from the ground up is justified.
- **Develop variations of sugarcane and other sugar-rich feedstocks:** Variations of sugarcane and other sugar-rich feedstocks that are suited for rapid growth in colder and drier climates are needed if these are to be considered for growing and processing in the US. It does not appear, however, that such research would provide any significant breakthroughs that would facilitate further commercialization of conventional ethanol as a transportation fuel. It is possible that such sugar-rich feedstocks would be applicable to other technologies, such as cellulosic ethanol production, so such research could also be considered for other technologies.
- **Investigate biomass-powered combined heat and power at existing ethanol facilities:** It is likely that the suppliers of corn for the production of ethanol would also be able to supply corn stover or other agricultural residues that may be able to displace at least a portion of the fossil fuel requirements of the typical ethanol production facility. This could reduce the greenhouse gas (GHG) footprint of the facility. However, such research would probably not provide significant breakthroughs that would facilitate further commercialization of conventional ethanol as a transportation fuel.
- **Extending Ethanol Blend Limits:** From a research standpoint, one of the most important priorities in this area should be investigations of the compatibility of higher alcohol/gasoline or higher alcohol/ethanol/gasoline blends with vehicle hardware and the effect on emissions. This could allow higher alcohol or higher alcohol/ethanol levels in gasoline, which would also be beneficial for the expansion of cellulosic ethanol. This research area is listed here for completeness, but this area is beyond the scope of topics covered under funding by the Alternative Fuel section of the PIER-Transportation Research Area. Such research would be more appropriately funded under the Vehicle Technologies section of the PIER-Transportation Research Area, or another outside agency or organization. In this regard, the PIER-TRA Vehicle Technologies section has recently initiated a program in this area that will be conducted by UC Riverside.

Research Recommendations

- It is unlikely that the production of starch- or sugar-based alcohols for fuel will expand significantly beyond current levels. Hence, it is not recommended that funds be allocated towards research for this technology unless this research could also facilitate the commercialization of another more promising technology. The development of biomass-powered combined heat and power technologies would probably be the research that would be most applicable to other technologies.

Biodiesel

Biodiesel is the second most prevalent alternative fuel in the US. FAME Biodiesel use has grown considerably over the last 10 years and the industry has reached some level of maturity. The important issues with expanding biodiesel use in California appear to be increased use of biodiesel and feedstock availability.

Status of Technology Development

- **Process Maturity:** The FAME biodiesel production process is fully mature and well understood. Biodiesel has expanded considerably in the past decade. The actual estimated US Biodiesel production by fiscal year (Oct 1 – Sept 30) for 2008 was 700 million gallons, up from only 2 million gallons for 2000.

Technological and Commercialization Gaps

- **Increased NO_x Emissions:** Biodiesel addition to diesel fuel is known to increase NO_x emissions. This is an important issue in California, since any changes in fuel regulations or fuel formulations must be done in a way that will not cause any increases or “back sliding” of any emission component.
- **Feedstock Limitations:** Currently, soybeans are the major feedstock for biodiesel production. Similar to ethanol, the use of soybeans for fuel production provides some competition for food uses. Soybeans also have many other uses and if the farmers can sell their soybeans at a higher price for these other uses then the biodiesel producer may not be able to get the supply they need. If all of the soybean oil, recycled restaurant grease, and other associated feedstocks were used to produce biodiesel, ~1.7 billion gallons of biodiesel could be produced each year, which is only ~5% of the current US on-road diesel usage.
- **Utilization Issues:** From a utilization standpoint, there are some issues with the use of biodiesel, including long term durability of systems with biodiesel, engine warranties, fuel quality, storage stability, and cold weather operability. While these issues are considerations with the use of biodiesel, they will probably not be the most significant issues for further commercialization prospects of biodiesel.

Potential Research Areas for Funding

- **Development of NO_x Mitigation Strategies:** In California, the mitigation of NO_x emissions from biodiesel blends is an important issue. The development of more cost effective fuel formulations for NO_x reduction would be an important help for biodiesel economics. This could include more effective additives or combinations of biodiesel feedstocks that are less prone to increasing NO_x emissions.

- **Find low cost feedstocks:** A low cost feedstock which doesn't have significant other uses would help to stabilize biodiesel supply. Jatropha, which is a bush of little commercial importance that can be grown on marginal lands, is one possible new candidate feedstock. The development of new feedstocks for oils would also facilitate the expansion of the hydrogenated vegetable oil process as well.
- **Determine the properties of any new potential feedstocks:** The properties of any new feedstocks need to be characterized with respect to impurities, the need for pretreatment as part of the production process and any associated waste products, the properties of the biodiesel produced, and the emissions when the biodiesel is used in an engine.

Research Recommendations

- Similar to starch- or sugar-based alcohols, it is unlikely that the production of FAME biodiesel will expand significantly beyond current levels, and it is not recommended that funds be allocated towards research for this technology unless this research could also facilitate the commercialization of another more promising technology. The development of low cost feedstocks, such as jatropha, would probably be the research that would be most applicable to other technologies.

Biochemical-Based Cellulosic Ethanol

Cellulosic biomass is expected to be the most significant source for production of ethanol, and other alternative fuels going into the next decade, in response to legislative initiatives. While cellulosic ethanol can be produced from a variety of different feedstocks, including agricultural residues, forestry and mill residues, municipal solid waste, and energy crops, it is more difficult and costly to produce cellulosic ethanol compared to converting sugars or starches to ethanol.

Status of Technology Development

- **Process Maturity:** Commercial ethanol production from cellulosic biomass is not available in the US yet. Several companies, including Abengoa Bioenergy, Iogen, BlueFire Ethanol, Mascoma, and POET, are working to develop commercial-scale biochemical ethanol production facilities. There are also a significant number of private companies developing and optimizing the enzymes and microorganisms necessary for biochemical production of ethanol from cellulosic feedstocks.

Technological and Commercialization Gaps

- **Production Costs:** The most significant technical barrier to the commercialization of these biochemical facilities is the lack of efficient and economical cellulose pre-treatment and enzymatic hydrolysis processes. Pretreatment is the most expensive operation within the production process. Cellulase enzymes and enzymatic hydrolysis are the second most costly element of the production process.
- **Utilization Issues:** As discussed above, ethanol has a number of limitations in terms of utilization, including a blend limit of 10% for conventional gasoline, the inability to use ethanol in pipelines, and its lower energy density.

Potential Research Areas for Funding

- **Reduce production costs:** Cost reductions are needed in harvesting, handling, storage, preprocessing, and processing.

- Pretreatment is the most critical area within the production process. Continued advances are needed in pretreatment technologies to improve sugar yields, reduce the chemical and energy requirements of the process, and minimize the production of inhibitory byproducts. A better understanding of the factors that promote the resistance to microbial destruction, or recalcitrance, in the biomass feedstocks is also needed to identify critical pathways in improving process cost effectiveness.
- Enzymes with better reaction rates, or specific activities, are needed to achieve high conversions with much less enzyme. Enzyme mixtures that can effectively release the hemicelluloses left in pretreated solids are also important for achieving the high yields needed for large-scale competitiveness.
- Consolidated bioprocessing can be used to incorporate enzyme production, hydrolysis, and fermentation into a single process step. More extensive process integration research can be utilized to generate integrated performance data and develop predictive mathematical models that can guide process optimization and scale-up. Research in process integration can require large or multidisciplinary teams and correspondingly larger program budgets.
- PIER should coordinate funding in this area with the already on-going work that is being funded by the US DOE. This would emphasize the study of unique processing requirements for California specific feedstocks including:
 - Develop and understand the pretreatment and resultant degradation for the specific feedstocks.
 - Fundamentals of cell walls of these materials.
 - Understand the unique enzymatic requirements for the hydrolysis of the pretreated product.
 - Optimize the integrated process of pretreatment, enzyme production, enzymatic hydrolysis, and fermentation for these feedstocks.
- **Develop improved feedstocks:** There is a need for high yielding and faster growing feedstocks which are drought resistant, have higher carbohydrate content, reduced fertilizer demand, and are less recalcitrance to biochemical conversion.
 - The DOE is very involved in funding cellulosic ethanol feedstock work. California should concentrate its research dollars on feedstocks that can be grown under the semi-arid and other climates found in California. PIER has an ongoing program with the California Department of Food and Agriculture to identify and evaluate food crops that can help identify California-based feedstocks suitable for further research.
- **Understanding overall sustainability and environmental impacts:** Understanding the overall sustainability and environmental impacts of energy crop production at the watershed level is another important area of research. The DOE recently issued a funding opportunity announcement to study this issue. Energy crop production encompasses crops planted exclusively for energy production. PIER should pay close attention to these studies in case there is the opportunity to leverage them towards cellulosic stocks native to California, or to crops expected to do well in marginal soils in California.
- **Vehicle Compatibility:** As discussed above, for ethanol use to expand to higher levels in conventional gasoline, the compatibility of higher alcohol/gasoline or higher alcohol/ethanol/gasoline blends with vehicle hardware and the effect on emissions must be investigated. Research in this area would be outside the scope of topics that would be funded by the Alternative Fuel section of the PIER-Transportation Research Area, and as

such would be more appropriate for funding under the Vehicle Technologies section of the PIER-Transportation Research Area, or another outside agency or organization.

Research Recommendations

- It appears that cellulosic ethanol will play an important role in the expansion of alternative fuels over the next 10 years and can utilize a broad range of feedstocks. As such, this is an area that PIER should allocate research funds to. Reducing production costs and developing improved feedstocks should be the highest priorities for research. As this technology is being funded extensively at the Federal level and in the private sector, PIER funds should be targeted toward development of feedstocks that would be most applicable for California and how to optimize the production processes for these feedstocks.

Thermochemical to Liquid

Gasification is a thermochemical production technique that can be used to produce a range of different fuels for transportation. The synthesis gas from gasification can be utilized for the production of diesel fuel via a Fischer-Tropsch (FT) process, ethanol via catalysis or fermentation, methanol, DME, or “green gasoline” from a methanol intermediate. The primary advantage of gasification is that it can utilize a very wide range of feedstocks compared to other processes. The disadvantages of gasification are that it is a complex and expensive process and that it is energy intensive.

Status of Technology Development

- **Biomass to Fischer Tropsch liquids:** There are a few projects either in-place or being developed for producing FT fuels from biomass. The companies developing or proposing biomass to FT facilities are Oxford Catalysts, Rentech, Flambeau River/NewPage, Stora Enso/Neste Oil, and FZK.
- **Thermochemical Processes for Ethanol Production:** A small number of facilities are believed to be under construction, but there are no commercial thermochemical cellulosic ethanol facilities currently in operation in the United States.
- **Methanol, Dimethyl Ether, and Methanol to Gasoline (MTG):** The production of methanol from syngas is a well understood, commercial process. The MTG technology is fairly mature. In the United States, there have been proposals to develop MTG facilities. Commercial coal gasification to methanol, DME, and MTG projects have recently begun operations in China. There are no commercial biomass gasification to methanol or gasoline via the MTG process being developed.
- **Jet Fuel:** The increased costs the airlines expect to see from the regulation of CO₂ emissions have driven the industry to put the production of jet fuel from renewable biomass on a fast track. Gasification followed by Fischer-Tropsch processing is one of the technologies being developed for renewable jet fuel production.

Technological and Commercialization Gaps

- **Economies of Scale:** Biomass to FT units will be constrained by the scale of biomass feedstock availability. The higher BTU content of coal and coke, along with the large-scale availability of these feedstocks, allows FT units based on these inputs to be built approximately 10 times larger and more economically.

- **Process Specific Reactors:** Most FT reactor focus has been on large-scale coal and natural gas based systems. Because of this, many vendors do not have offerings at the scale needed for biomass and have not spent time and effort developing an optimized reactor for this smaller system.
- **Scale-Up:** As with most developing technologies, issues tend to arise that are not accounted for when moving from the demonstration or pilot scale to commercial operation.
- **Catalyst Shortfalls:** Most improvements in FT catalysts in the last 80 years have been largely incremental and most research has focused on coal-based syngas. Developing catalysts with higher per pass conversion, better selectivity, and lower sensitivity to impurities would improve the overall process economics.
- **Biomass Quality:** Building a large biomass to FT plant will require obtaining feedstock from different sources, each of which may vary in size and composition. This variation can cause gasification problems and require significant pre-processing, adding to the overall system costs. The preprocessing requirement for some fuels, such as renewable jet fuel, may require even greater levels of processing due to the more stringent requirements on the final fuel.
- **Impurities and Gas Cleaning:** Due to the specific requirements of current FT catalysts, syngas must be cleaned to very tight specifications. The most pressing issues are tar removal and clean-up temperatures. Many tar removal technologies are either ineffective or very detrimental to process efficiency. Many gas clean-up processes also require cooling the syngas from gasifiers exit temperatures to near 100 °F before reheating the syngas back to 500 °F for feed to the FT unit.

Potential Research Areas for Funding

- **Economies of Scale:** There is a need to develop much smaller gasification/FT units that can be operated economically, since the available biomass within a reasonable transportation distance cannot support the large units designed for natural gas or coal.
- **Scale up:** Demonstration and pilot scale units need to be developed to explore issues which may arise when designing and operating a commercial size unit.
- **Biomass Quality:** Pretreatment processing of the biomass prior to gasification may be an option for producing a more uniform product for the gasifier. The impact of pretreatment of biomass feedstocks on the subsequent gasification processing could be evaluated.
- **Selective FT Catalyst:** There is a need to develop FT catalysts with higher per pass conversion, lower sensitivity to impurities and/or process conditions, and better selectivity for carbon number, which dictates the type of products produced (the split between gasoline, jet, and diesel boiling range compounds). Meeting these objectives would require the successful manipulation of the FT chain-growth mechanism, which has not been achieved as of yet. Monolithic and edge coated FT catalysts are being investigated for selective FT synthesis.
- **FT Process Intensification:** Process intensification is the consolidation of multiple process steps into a fewer number of units. This helps to improve efficiency and lower overall costs. Options include development of economic reactor technologies for syngas conversion based on process intensification, catalyst/reactor integration, and heat management to improve the viability of biomass-based FT systems. Development of

modular-type reactor systems could help improve the viability of distributed biomass gasification plants.

- **High Temperature CO₂ and Sulfur Removal:** Syngas produced from biomass conversion includes a large fraction of CO₂ and may include some amount of sulfur. The presence of CO₂ can have detrimental effects on syngas conversion, and even small amounts of sulfur can be poisonous to FT catalysts. High temperature CO₂ removal using advanced sorbents or membranes could improve the process efficiency by reducing the cooling and reheating requirements. High temperature sulfur removal has been demonstrated using circulating beds of solid sorbents. None of these technologies are commercially available.
- **Tar Removal:** Tar production during the gasification process is another contaminant which must be removed prior to the FT unit and better methods for this removal are needed.
- **Catalytic Biomass Gasification:** In addition to traditional noncatalytic gasification processes, catalytic gasification of biomass can be used to lower the operating temperature, making the process more economically feasible. Rapid deactivation by tar formation at the lower temperatures of catalytic gasification has led to the search for more tar-resistant, but still active, gasification catalysts.
- **Steam Hydrogasification Reactor (SHR):** Hydrogasification combines a SHR with a Steam Methane Reformer (SMR) to produce a syngas for Fischer-Tropsch processing. Since the process does not require oxygen, which is very expensive, or air, which significantly decreases the calorific value of the product gases because of the high nitrogen content, SHR may be more economical to produce at a smaller scale. Also, because SHR uses a wet feedstock, there is no need for pretreatment to dry the feedstock.
- **Feedstocks:** Similar to the recommendation made for cellulosic ethanol it is recommended that California concentrate its Fischer-Tropsch efforts on California feedstocks.
- **Market Conditions:** Specific market conditions would also be helpful in making this type of project economic. Having low or negatively priced feedstock (i.e., with a tipping fee) would be helpful to make biomass FT projects attractive. Integrating the processing and upgrading for a FT process with an established refiner may reduce capital and operating costs. Co-firing of Biomass with coal or petcoke would reduce the environmental impact relative to straight fossil fuel feedstocks while taking advantage of the economy of scale that comes with a fossil-based facility, although this would not directly represent a renewable biomass conversion technology. Taking these three factors into account, it appears that locating a biomass to FT facility near a large metropolitan area and using urban wood wastes could be the most economic arrangement for a biomass to FT facility.

Research Recommendations

- The development of thermochemical processes could play a key role in optimizing the production of fuels for transportation. Thermochemical processes can utilize a wider range of feedstocks compared to biochemical processes and can also be integrated into processes for combined heat and power. Synthetic alternative fuels produced from thermochemical processes can also provide liquid fuels that would be very compatible with the anticipated vehicle technology mix going out at least 20 to 30 years into the future. This includes applications such as renewable jet fuel, which is now attracting

interest from the public and private sectors. Given these considerations, it is recommended that PIER allocate funds toward research efforts in gasification or other thermochemical technologies. Gasification processes tend to be larger in scale and more complex compared to other technologies, hence the viability of gasification processes may hinge on having a sufficient supply of feedstock within a reasonable transport distance of the facility. Thus, it will be important to determine if optimal locations can be found within the State that provide a sufficient quantity of feedstock within a reasonable transport distance, as discussed above. If such locations can be identified, then further research into improving gasification production technology could be of merit. Alternatively, technologies that can be built at a smaller scale, such as hydrogasification, may merit further research and development.

Pyrolysis

Pyrolysis is another thermochemical process that can be used to convert biomass from a wide range of sources to a liquid fuel. Pyrolysis differs from other thermochemical processes in that it is done in the absence of oxygen and at lower temperatures, producing a gas-phase product, a pyrolysis oil, and a solid biochar. The resulting pyrolysis oil is a fairly low quality product that requires considerable upgrading to meet transportation fuel quality specifications. The biochar can be potentially used as a soil amendment and for carbon sequestration.

Status of Technology Development

- While there have been limited niche successes, there has been no widespread commercialization of pyrolysis as yet. There are four companies that appear to be most heavily engaged in commercialization efforts today: Dynamotive, Ensyn/UOP/Envergent, BTG, and PyTec, with Dynamotive being the most active. Upgrading pyrolysis oil to high-quality hydrocarbon fuels has been demonstrated at a non-commercial scale.

Technological and Commercialization Gaps

- **Pyrolysis Oil Quality:** The quality of raw pyrolysis oil is very poor, requiring extensive upgrading before it can be used as an on-road transportation fuel. While technologies exist to do this, the high cost and low yield have typically made conventional options too expensive.
- **Small Sizes:** A large-scale pyrolysis oil plant of 100,000 tons (roughly 2200 barrels per day) is equivalent to 0.5 to 2% of the input to a typical crude oil refinery. Refiners will likely be reluctant to make major changes to their process to accommodate such a small amount of feedstock. In addition, new refinery applications (such as hydrocracking and hydrotreating) are typically built in the 10,000 barrel per day range or higher due to economies of scale.
- **Lack of Integration with Petroleum Refiners:** The most logical route for upgrading bio-oils would be partnership with petroleum refiners. Partnerships such as those that some oil companies have established for the production of other biofuel routes would be useful, such as BP (with Verenium), Shell (previously in a partnership with Choren, now dissolved), and ExxonMobil (with Synthetic Genomics).

Potential Research Areas for Funding

- **Improve knowledge of complex pyrolysis reactions:** Fundamental studies of the complex reactions are required to develop a unified theory to predict pyrolysis behavior for different feedstocks.
- **Catalytic (in-situ) pyrolysis:** Noncatalytic pyrolysis does not produce fungible gasoline and diesel products. When catalysts are used in pyrolysis, alkylation, isomerization and reforming reactions can take place to produce alkanes and aromatic and cyclic compounds, major components of diesel and jet fuel.
- **Improve upgrade catalyst formulations and reduce hydrogen requirements:** The petroleum refining industry continues to look at ways to develop and improve upgrading catalysts, which are catalysts designed to upgrade lower quality materials into higher quality products. These improvements could include higher yields and/or greater tolerance of poor quality feedstocks. Future research in this area, not necessarily related to pyrolysis oils, could be of benefit to the commercialization of pyrolysis.
- **Upgrading bio-oil using syngas derived from biomass gasification:** To operate a stand-alone pyrolysis plant, it may be necessary to build a small gasifier to supply syngas to the adjacent pyrolyzer to achieve self-sustained operation. Using syngas as a hydrogen source for bio-oil hydrotreating has not been explored and the interactions between CO and bio oils needs to be better understood.
- **Enhancing the feedstock flexibility of pyrolysis units:** Improving reactor performance to allow a wider range of feedstock types and reducing sensitivity to size and content would lower the cost of raw materials and improve yield.
- **Effect of alkaline cations in biomass feedstock:** There is a need for a more systematic understanding of the role of different alkaline cations, as well as the alkaline cation concentration, on the pyrolysis reaction. The introduction of different catalytic materials could be used to alter the product bio-oil composition.
- **Continue research on novel upgrading strategies, such as microwave-activated pyrolysis:** More novel upgrading methods have the potential to make major step changes in the cost or equipment required to perform upgrading. Microwave-activated pyrolysis is an example of one such technology.
- **Medium scale conversion systems:** Pyrolysis seems to offer a potentially attractive scale match for medium scale conversion systems (e.g., 50 to 250 tons/day) that could be deployed in a distributed strategy for storable liquid fuel production. This could address some fundamental drawbacks with long-distance transport of typically bulky biomass feedstocks to large centralized biomass conversion facilities.

Research Recommendations

- Pyrolysis is part of the suite of thermochemical technologies that PIER should allocate research funds towards. The smaller-scale, less expensive nature of pyrolysis in comparison to other thermochemical processes provides useful advantages that help offset the poor quality of the pyrolysis oils that are produced. The potential of utilizing pyrolysis to “densify” raw biomass to pyrolysis oil at distributed, remote locations, which can subsequently be transported to a centralized processing/upgrading conversion facility, appears to merit further investigation. Economic analyses of the viability of such a strategy could be tied to the study recommended above on identifying optimal facility locations based on feedstock distribution. The upgrading of product oils to transportation-quality liquid fuels is the most significant technical challenge for pyrolysis and it is suggested that this be the primary emphasis of any pyrolysis research funding. The

petroleum industry continues to look at ways to develop upgrading catalysts that can improve yields and be more tolerant of poor quality feedstocks. Some strategies that could be used to facilitate upgrading include utilizing syngas from a small gasifier, in-situ catalytic pyrolysis, or the development of more novel upgrading methods, such as microwave techniques.

Renewable Diesel

The hydrogenation of vegetable oils and animal fats uses more traditional refining methods of hydrotreating to produce diesel fuel. The finished product is similar to traditional diesel, with a hydrocarbon mixture of isoparaffins and paraffins, which is compatible with the traditional pipeline, fueling, and vehicle infrastructure.

Status of Technology Development

- There are currently several facilities producing renewable diesel fuels on a commercial basis around the world. The process has been commercialized in Europe, where the economics are more favorable, but not in the US as of yet. Neste Oil has one of the most advanced renewable diesel programs, with two existing facilities in Finland and two more facilities in Singapore and Rotterdam, respectively, being built. Other companies working on the development of renewable diesel include ConocoPhillips, BP, UOP, Petrobras in Brazil, Nippon Oil, and CanmetENERGY.
- **Jet Fuel:** Hydrotreating Vegetable Oils in another technology being developed for the production of renewable jet fuel that has been the subject of a number of projects backed by the airline industry or government entities.

Technological and Commercialization Gaps

- The use of the technology will be driven largely by the economics of the process, including the cost of vegetable oils and animal fats, if they are available in sufficient quantities to sustain a continuously operating process, the cost/availability of hydrogen, and the capital required to develop a vegetable oil and/or animal fat hydrotreater as a standalone facility or at an existing petroleum refinery. The availability of excess capacity for hydrotreating in existing refineries will be another important consideration.

Potential Research Areas for Funding

- **Feedstock Availability and Cost:** The development of lower cost feedstocks, similar to those suggested for FAME biodiesel, is an important area of research. Such research would be useful for the development of the biodiesel market as well.
- **Co-processing vegetables oils and/or animal fats with diesel fractions:** A lower capital cost option would potentially be the hydrotreating of vegetable oils and/or animal fats with diesel fractions simultaneously. This would likely take place within an existing petroleum refinery and require modifications to the existing diesel unit. This strategy would also likely reduce the life of the hydrotreating catalyst if pre-treatment of the vegetable oils and/or animal fats is not performed. Research focus on hydrotreating catalysts that can handle blends of petroleum fractions and vegetable oil and/or animal fat at the same time may be of interest.

- **Improved catalysts: Whether the vegetable oil or animal fat is hydrogenated in a separate** unit or co-processed with the diesel fractions, the activity, stability, and useful life of the catalysts needs to be improved.
- **Understanding contaminant impacts on production:** Understanding the influence of contaminants in the processing and controlling issues such as corrosion could help in improving the production process.

Research Recommendations

- Hydrotreating has the advantage of being a well developed refining process that produces a fuel that has properties of a high quality diesel or jet fuel. While some of the research recommendations for renewable diesel are unique to hydrotreating vegetable oils, some of the other suggestions would have applications towards other technologies as well. The development of feedstocks applicable to renewable diesel could similarly be used in the production of other fuels, such as biodiesel. The development of the ability to co-process vegetable oils and/or animal fats would also potentially facilitate the co-processing of other feedstocks such as pyrolysis oils. Similarly, improving the activity, stability, and useful life of catalysts for vegetable oils, would probably also provide benefits for the processing of either traditional petroleum streams or other biomass-related materials. Given the emphasis on upgrading processes and feedstock development, it is recommended that PIER funds also be allocated toward the development of renewable diesel and its associated feedstocks.

Algae

Algae-based fuels have many promising characteristics. Algae can provide much higher oil yields than more traditional terrestrial crops such as soybeans or palm oils. Algae can be grown in a variety of aqueous environments, including in water sources on marginal lands unsuitable for food crops. Thus, algae do not compete directly with food supplies. Interest and investment in algae-based fuels is rapidly growing. Although much research is still needed to make algae-based fuels viable transportation substitutes, algae-based fuels could represent the next generation of fuels that follow those derived from cellulosic ethanol.

Status of Technology Development

- Currently, there are no commercial algae production facilities because research has not yet demonstrated a viable production method that can be sustained on a continuous basis, as toxic by-products interrupt the algae growth. Considerable basic and applied R&D is needed to overcome the current technical barriers for algal-based fuel production and the cost effective production of algae is a good 10 years away. Nevertheless, investment in the development of algae-based fuels is expanding in both the private and government sectors. ExxonMobil, in collaboration with Synthetic Genomics Inc., and Chevron, in collaboration with Solazyme, are both working on the development of algae-based fuels. The US DOE and NREL have a number of algae research projects underway, and a National Advanced Biofuels Consortium has just been funded to be led by NREL and the Pacific Northwest National Laboratory. A number of small venture companies are also active, with Algenol Biofuels Inc., Solazyme Inc., Sapphire Energy, and Univenture and Algaeventure all receiving funding from the Federal government to develop pilot plants

or develop new production methods. Algae is also being developed as a potential feedstock for the production of renewable jet fuel.

Technological and Commercialization Gaps

- **Stability of large scale cultures:** Ideally, one wants to grow a specific algal strain that is known to be a good source for fuel production. This can be difficult to accomplish, particularly in an open pond system, because of contamination with algal strains native to the area, or predators and/or pathogens, which could be destructive to a specific algal strain.
- **Nutrient sustainability and management:** Algae require a sustainable supply of low cost nutrients to achieve rapid growth. Nutrient supply issues can have a sizeable impact on cost, sustainability, and production siting. Issues relating to this include managing the nutrient levels and the cost and source of the nutrients. The most critical nutrients include nitrogen, phosphorous, iron, and silicon.
- **Water management:** The cultivation of algae requires large quantities of water. To improve the overall production effectiveness, designs must be developed to conserve water and to optimize and control the water recycle. These systems must also monitor changes in water quality due to evaporation and properly treat entering and exiting water.
- **Harvesting, dewatering, extraction, fractionation, fuel production:** The costs of all of these steps must be reduced, some substantially, to make fuels from algae economic.

Potential Research Areas for Funding

- **Development and optimization of algae strains:**
 - **Developing stable, competitive production strains:** The strains need to be resistant to attack from pervasive algal predators and pathogens. This represents one of the most important areas of research for algae strains. Other possible options to improve algae culture's susceptibility to predator invasion include chemical treatments and environmental or physiological adaptations.
 - **Wider growing conditions:** The stains need to be able to grow at a high rate over a wider range of ambient temperatures. Optimizing strains of heterotrophic algae, or algae that are grown in the dark, would also allow for greater diversity in the conditions that could be used for algae for fuel production. Identification of species that can better utilize shorter wavelengths to grow would also improve cultivation, since algae growth rates are often limited by light penetration into the ponds and shorter wavelengths will have greater penetration depths. Strains that can provide good yields with reduced water and nutrient levels would also be useful.
 - **Basic research in multi-trophic, molecular-level algal ecology:** Some algae species may process the nutrients more efficiently, but not produce the desired concentrations of oils and lipids, while their waste products may be efficiently converted to oils and lipids by other species.
 - **Higher percent of total biomass as oil:** The strains need to produce higher concentrations of lipids, which are the precursors that can be processed to produce fuels.
 - **Faster growth, higher biological efficiency:** Strains need to be developed that have faster growth rates and greater biological efficiency.
- **Cultivation of Algae:**

- **Better control of culture stability:** Understanding the health and composition of the ponds used for growing algae remains an important element. Automated biological and chemical monitoring should be incorporated into any research geared toward the cultivation of algae. The information obtained from such monitoring would also be useful in the early identification of invasive species, predators, pathogens, the optimization of the chemical treatment of the pond, and in understanding the pond speciation, ecology dynamics, and frequency of contamination events. The systems and strains must also be sufficiently constrained to minimize the risks to biodiversity from genetically modified organism (GMO) strains of algae.
- **Management of water and nutrient requirements:** The management of the supply and the use of nutrients in the growth process is an important aspect of cultivation. Research in optimizing the control of nutrient levels, finding inexpensive sources of nutrients, and developing strategies to recycle nutrients would all improve the production process. Managing the water demands for large cultivation systems is also important. Additional research in designing systems to conserve water, optimizing and controlling water recycle, treating entering and exiting water, and addressing changes in water quality due to evaporation would be useful in this regard.
- **Downstream processing of algae for major cost reductions:**
 - **Understanding the fundamental aspects of algae relating to downstream processing:** This would include research to understand the impacts of processing on cell wall composition. Studying and understanding lipid genesis, composition, and structure could also be useful in optimizing extraction yields.
 - **Developing improved systems for downstream processing:** The technologies for extracting algae are expensive in terms of either equipment costs or energy requirements. Systems or engineering improvements in these areas would improve the economic viability of algae production as a whole. This could include the development of multitasking extraction processes or improved methods for dealing with water in the downstream processes.
- **Use of algal residuals after the lipids or other desirable fuel precursors have been extracted:** This could include the processing of the residuals to provide energy to reduce the processing energy cost or the development of valuable co-products. This would help improve the overall economics of the processing.
- **Lifecycle analysis of energy and carbon in selecting preferred fuel conversion technologies:** As for all alternative fuel production methods, lifecycle analysis of energy and carbon must be considered in selecting the optimum method for fuel production.
- **Integration issues and opportunities for algal cultivation facilities co-located with industrial CO₂ sources and/or wastewater treatment facilities:** Since wastewater and CO₂ can serve as the main nutrient sources for algae, co-locating the algae growing near these sources could substantially reduce the growing costs.

Research Recommendations

- Algae-based fuels may represent the next generation of biochemical based fuels that would follow those derived from cellulosic ethanol. The increase in funding at the Federal level and the number of companies (many based in California) becoming involved in the study and development of algae-based fuels is one important indicator of

the optimism. It is recommended that research toward the development of algae-based fuels be supported by PIER as a medium term transportation fuel strategy, with implementation into the marketplace out 10-20 years. This could include research spread out among the different main areas for funding described above, including the development and optimization of algae strains, the cultivation of algae, or downstream processing or coprocessing of algae.

Other Technologies

A number of other technologies were reviewed that included more mature technologies, such as CNG and LPG, that are not likely to expand market share going into the future, and technologies that still require significant research to become commercially viable, such as hydrogen and other technologies. The recommendations for these technologies are reviewed below.

Natural Gas/Anaerobic Digestion

Natural gas has been used in vehicle applications for several decades, but the vehicle availability and refueling infrastructure are still limited. Additionally, natural gas is currently produced from fossil fuel sources. For this roadmap the production of methane, the principal component in natural gas, from anaerobic digestion of organic matter was examined. This process occurs in landfills and is also used in wastewater treatment facilities, dairies, and animal feeding operations. Producing methane via anaerobic digestion has several limitations, including the poor quality of the gas and competition with the typical use for electricity/energy generation. Given these limitations, it was concluded that anaerobic digestion would not likely make a significant contribution towards alternative transportation fuels. Natural gas can also be produced via other biochemical or thermochemical processes or harvested from methane hydrates, but even for these other methods, the issues with vehicle availability and infrastructure would likely limit this technology to niche markets. Considering all of these factors, it is recommended that PIER funds not be allocated toward research in natural gas for transportation applications.

Liquefied Petroleum Gas (LPG)/Propane

LPG has similar limitations as natural gas with respect to vehicle availability, refueling infrastructure, and the fact that LPG is currently produced from fossil fuel sources. The development of LPG for transportation applications is less developed than that for natural gas vehicles (NGVs). Although there is some specific research into producing propane from biological sources, this research is still in its infancy and mostly being conducted at a university level. Also, many of the methods that would be used for the production of propane can also be used to produce fuels that are more similar to gasoline and diesel fuel that could be used in existing vehicles and with the existing infrastructure. Based on the limitations with vehicles and infrastructure, and the lack of unique production advantages, it is recommended that PIER funds not be allocated toward LPG research for transportation applications.

Hydrogen

There are still critical barriers to the continued development of hydrogen as a transportation fuel and a majority of the goals in a recent 5 year collaboration between the DOE and major

automobile manufacturers were not met. Nevertheless, it appears that hydrogen could play a role as a transportation fuel in the longer term, 2040 to 2050 timeframe. California is already investing in a hydrogen fuel infrastructure, and there is also some industry investment in vehicle technology. It appears unlikely that hydrogen will have a significant impact as a transportation fuel over the next 10-15 years. Overall, it is recommended that hydrogen be included in the portfolio of fuel technologies to be supported by PIER. Hydrogen should be considered a longer term transportation solution, targeting a time horizon in the 2030-2050 period. PIER should continue to monitor developments in hydrogen production techniques and vehicle technology. Key areas for PIER funding should include fuel cell technology and hydrogen production techniques, such as solar energy. The funding for development of hydrogen fuel production technologies is most appropriate within the fuels section of the PIER-Transportation Research Area, while the funding of fuel cell or hydrogen internal combustion engine related projects is more appropriate for funding under the vehicle technology section of the PIER-Transportation Research Area.

Carbon Dioxide Conversion to Hydrocarbons

This technology is based on the conversion of CO₂ to a series of hydrocarbons when it undergoes an electrocatalytic reaction inside a confined carbon micropore with noble metal nanoclusters. Research into this technology is being conducted at a small number of universities throughout the world. This research is in the very preliminary stages in terms of commercialization, and many more years of basic research are required to determine if any such method would be viable for advancement to the pilot stage. Overall, it appears that other technologies are more viable for the timeframe extending out until 2050, so this area is not recommended for PIER funding as a long term fuels technology. This area is more appropriate for Federal funding, with the potential for PIER to reexamine funding opportunities if significant breakthroughs are made in the technology.

Fuels from Sunlight Program

This is a recently initiated DOE program focusing on generating fuels directly from sunlight (DOE 2009a). The initial grant of \$122 million in funding was awarded to a team of researchers from the California Institute of Technology (Cal Tech), Lawrence Berkeley National Laboratory, as well as a number of other Universities. The goal of the center is to develop an integrated solar energy-to-chemical fuel conversion system and move this system from the bench-top discovery phase to a scale where it can be commercialized. Research will be directed toward developing the functional components necessary to assemble a complete artificial photosynthetic system, integrating those components into an operational solar fuel system, and developing strategies for scale-up from laboratory to commercial viability. While development is still needed in this area before it is commercially viable, it appears that there is good momentum at the Federal level to move this program forward. As such, it is recommended that PIER direct some of the funding for its long term development efforts to this area. Given the level of funding already being provided by the Federal government in this area, PIER should look for specific niches to fund/supplement within the overall portfolio of this program. This niche could be within the solar energy area, which would potentially also have broader implications towards hydrogen production and the development of hydrogen fuels as a long term transportation solution.

1 Introduction

The expanded use of alternative transportation fuels is becoming a more critical strategic objective on both a state and national level. Increased use of alternative transportation fuels can provide benefits in reducing oil dependency, air pollution, and, if the feedstocks are sustainable, greenhouse gases (GHG). At the California state level, a number of initiatives and legislative measures are promoting expanded use of alternative transportation fuels. The State Alternative Fuels plan, developed under Assembly Bill 1007 (Pavley, 2005), presents strategies and actions needed to increase the use of alternative non-petroleum fuels (CEC/CARB, 2007). This includes milestone goals for the years 2012, 2017, and 2022, with a longer term plan for a multi-fuel transportation fuel infrastructure in California by 2050. Assembly Bill AB 118 (Nunez, 2007) created a new alternative and renewable fuel and vehicle technology program to be administered by the California Energy Commission (CEC), while AB32 (Nunez/Pavley 2006), the Global Warming Solutions Act, requires California to develop regulations that will reduce greenhouse gas emissions to 1990 levels by 2020. The California Air Resources Board is developing and implementing a Low Carbon Fuel Standard (LCFS) that will reduce the carbon intensity of fuels, measured on a full lifecycle basis, by 10% by 2020 in response to Executive Order S-01-07 (Schwarzenegger, 2007). Additionally, the Bioenergy Action Plan, developed in response to California state Executive Order S-06-06 (Schwarzenegger, 2006), establishes goals for California to produce a minimum of 20% of its biofuels within the state by 2010, 40% by 2020, and 75% by 2050 (BIWG, 2006). At the Federal level, the Energy Policy Act of 2005 (US Congress, 2005) and the associated Renewable Fuels Standard (RFS1, 2007) contain a number of provisions that promote the development of renewable fuels, including a requirement that 7.5 billion gallons of renewable fuels are produced in the U. S. by 2012. In 2010, EPA revised the regulation requirement to 36 billion gallons of renewable fuels being produced in the U.S. by 2022, with 21 billion gallons of this limit being produced by advanced technologies (RFS2, 2010).

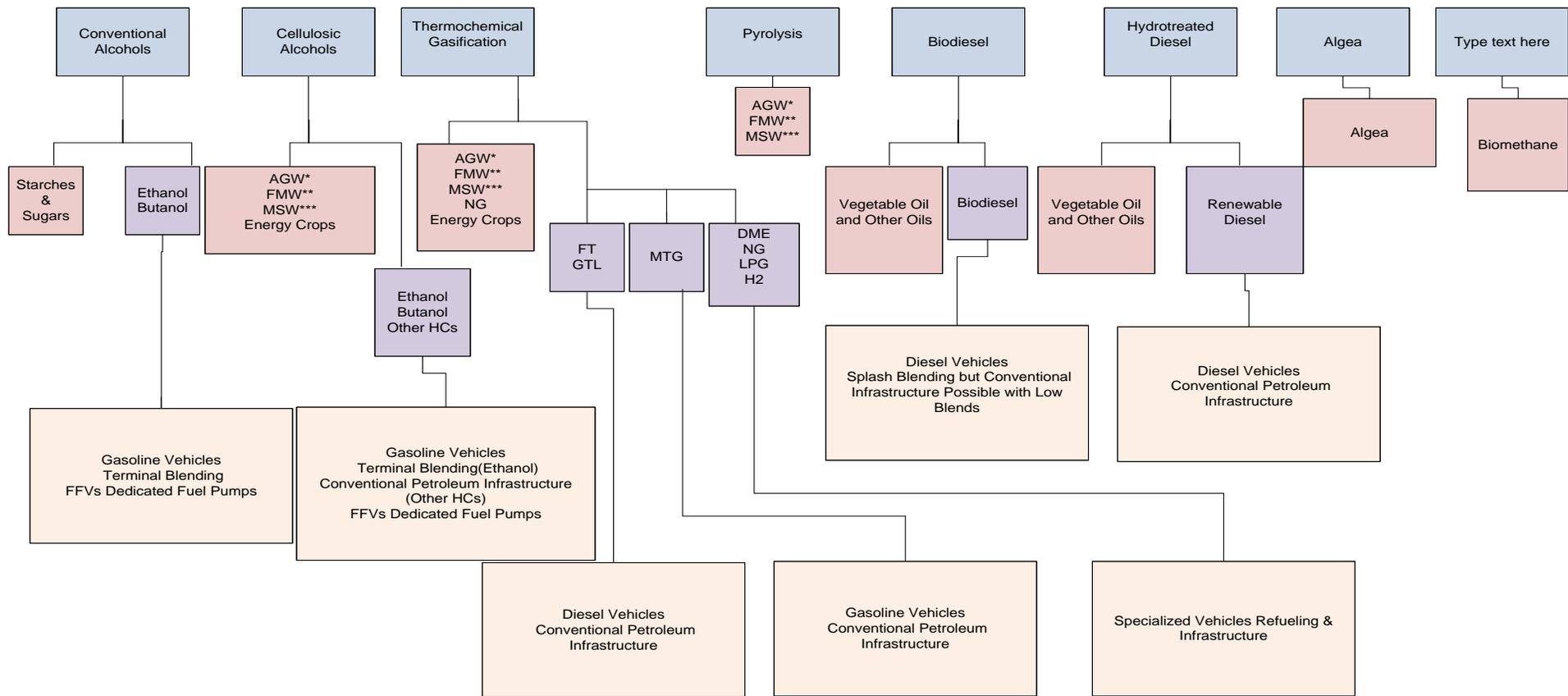
With such aggressive implementation goals for alternative transportation fuel use, it is important to understand what alternative fuel resources are available, what their limitations are, and what additional research is needed to make their implementation successful. A number of alternative fuels have already been developed for transportation applications including ethanol, biodiesel, natural gas, propane, and others. Of these fuels, ethanol is the most extensively utilized, currently representing 10% of California's gasoline supply. More than 95% of the ethanol used in California is either imported directly or made from imported corn, however. Biodiesel and natural gas are also fairly well developed fuels, although they have generally been applied at a smaller scale either in centralized fleet applications or, for biodiesel, in the statewide fuel pool at a 2% level in Minnesota. California is evaluating the expanded use of biodiesel within the state. It is expected that these developed fuels will be able to provide the predominant portion of the expanded alternative fuel needs in the near-term, but these fuels will also have limitations in terms of feedstock, production availability, or other infrastructure issues. Other fuels, such as hydrogenated renewable diesel fuels or synthetic gasoline or synthetic diesel fuels are less mature technologies, but may provide advantages over the long term in terms of infrastructure compatibility or broader feedstock applicability.

To meet the statewide and national objectives set for alternative fuels use requires continuous research and development. Alternative Fuels research development and demonstration (RD&D)

is a diverse, rapidly evolving, and highly technical field. To effectively utilize research funds in this area, it is important to establish goals and identify areas where research funding will provide the most value. The Public Interest Energy Research-Transportation Research Area (PIER-TRA) contracted with CE-CERT to develop a research roadmap to help guide PIER investment and decision making in a manner consistent with State transportation energy policy and goals, as described in the State Alternative Fuels Plan and the Bioenergy Action Plan for California. The roadmap is intended to assist the PIER-TRA program in defining research activities to remove barriers to deploying alternative fuel technology and infrastructure. The roadmap was developed through a series of reports designed to cover the main necessary elements for the roadmap. This included white papers covering the following topics: (1) a snapshot evaluation of the state-of-the-art of technological development of various alternative fuels, including feedstocks, production, and distribution and infrastructure (2) recommendations for fuels of the greatest interest for future PIER R&D funding, and (3) an analysis of the areas of funding that should be supported to reduce the gaps preventing commercialization [gaps analysis]. This document represents the research roadmap this is a culmination of all of these elements.

Structure of This Roadmap

The organization of this report is based on separate evaluations of different alternative fuels and alternative fuel technologies. The chapters and associated evaluations are done by a combination of the type of fuel and/or the production technology category, for example, cellulosic ethanol, biodiesel, or gasification for production of Fischer-Tropsch diesel fuel. A schematic of the different fuel technologies evaluated, their typical feedstocks, and their vehicle and infrastructure requirements is provided in Figure 1-1. It is worth noting that the fuels and fuel technologies being reviewed for this roadmap are combustion-based, as opposed to technologies used for electric vehicles, since the research objectives of the PIER Transportation Alternative Fuels Research Area are specific to combustion fuels. For each fuel technology, an overview of the development of the fuel is provided, including what feedstocks the fuel is made from, the commercialization level of the production process for the fuel, and the development of the infrastructure and distribution system needed for the fuel. The limitations of each fuel are then discussed in the areas of feedstocks, production processes, and distribution infrastructure. Environmental considerations such as lifecycle greenhouse gas emissions and vehicle emissions are then discussed. Ongoing research related to the fuel technology is then discussed. Research recommendations are then made for each fuel based on its current level of development, its technical limitations and commercialization gaps, ongoing research efforts, and its prospects for future expansion. A separate evaluation of the potential availability of cellulosic feedstocks in the US and California is also provided upfront since feedstock availability will provide the basis for the growth potential and expansion of all alternative fuels.



* AG=Agricultural Waste ** FMW=Forest and Mill Waste *** MSW=Municipal Solid Waste

Figure 1-1: Schematic of the Fuels and Fuel Technologies Reviewed in This Report.

2 General Overview of Alternative Fuel Feedstocks

2.1 Introduction

One of the most important criteria in evaluating the potential for an alternative transportation fuel is to determine the extent to which the use of the fuel can be expanded. While expansion of use for an alternative fuel can be limited by a number of factors, including costs, technological development, and infrastructure, one of the most important criteria for long term sustainability is the availability of an adequate feedstock supply from which the fuel can be produced. Since some fuels are produced from a more narrow range of feedstocks, while other fuels can be produced from a wide range of feedstocks, it is important to provide an overview of the feedstock potential for various fuels and technological processes. This chapter discusses the availability of feedstocks from a broader perspective for the applicable fuels. The potential and limitations for specific fuels/technologies is discussed in subsequent chapters.

In the broadest sense, an alternative fuel is any fuel which can be used to replace, or reduce the consumed quantity of, petroleum-based gasoline and/or diesel fuel. Potential feedstock sources include: (1) any biomass, such as any living plant, manure, animal fats, and algae, (2) natural gas including biogas, (3) propane/liquefied petroleum gas (LPG), (4) carbon dioxide, and (5) water, among others. Any fuel which can be produced from a biological source is bio-based. If the biological matter can be replaced as fast as it is used to make fuels and other products then the fuel source is renewable. In contrast, fossil fuels require very long periods of time to form, and hence are limited to what are currently in the ground and recoverable.

The feedstocks for the various processing options depend upon the technology for producing the desired final fuel. Some processing technologies such as pyrolysis, gasification, and cellulosic ethanol can utilize a wide range of feedstocks. Other processes such as fermentation to produce ethanol or the production of biodiesel from oils utilize a narrower range of feedstocks. On the other hand, these represent some of the most prevalent renewable fuels currently being marketed, and hence the feedstocks for these processes are characterized separately. Other alternative fuels are more traditionally associated with petroleum industry processes. This includes natural gas, which is found in vast quantities in underground reservoirs, and propane or LPG, which is available as a byproduct of the crude oil refining processes and natural gas production. While both natural gas and LPG can be made from other processes, such as gasification, the production and availability of these fuels from traditional sources is also of importance and is profiled separately. Coal can be converted to a liquid fuel by the Fischer-Tropsch process; thus, it also fits under the broad definition of an alternative fuel. Coal, however, has major limitations in that it is not renewable and it is environmentally destructive to harvest or mine.

The availability of all these categories of fuels will be discussed in this chapter, including feedstocks that constitute biomass that can potentially be used for alternative fuels, plus the availability of natural gas and coal. The bio-based broader categories include agricultural residues, forest and mill residues, energy crops, municipal solid waste (MSW), and algae. These sources represent the total amount of renewable feedstocks that might be available for use as a transportation fuel. The potential to utilize the full potential of the available biomass will depend on the development of different production technologies, as discussed in subsequent chapters.

2.2 Biomass Availability in the United States

Estimates of the available bio-based material are typically expressed in bone dry tons per yr (bdt/yr) and are labeled as biomass. There are many estimates in the literature of the total quantity of biomass available throughout the world and in specific areas of the world, such as the United States (US), specific US states, or specific areas within a state. The estimates vary depending upon the input assumptions. Some of the assumptions include (1) what quantity of the total biomass is available for fuel production, (2) what price will make the biomass more attractive for fuel production than for other uses, (3) what is the cost of harvesting and transporting this biomass, (4) what is the cellulose and water content of the biomass, and (5) what are the expected returns for energy crops versus conventional crops. (Energy crops are plants that are specifically processed to produce fuels rather than to produce food. Additional information about energy crops will be discussed later.)

Gronowska et al. (2009) reviewed 15 studies estimating the availability of lignocellulosic biomass quantities in the US and/or Canada. The US studies that include economic considerations estimated annual biomass availability to range from 6 to 577 million bone dry metric tons/year (mbdmt/yr) depending upon the offered price. US estimates based strictly upon inventory, irrespective of the costs of utilizing the material, range from 190 to 3849 mbdmt/yr.

The significant differences in the estimates are largely due to the number of biomass categories included, whether economic considerations are incorporated, assumptions about energy crop yields and land areas, and the level of optimism in the assumptions of the study. Gronowska et al. (2009) also noted that some estimates are based upon a top-down approach while others are based upon a bottom-up approach. For the top-down approach, estimates are based upon aggregate national estimates based on national average estimates of yields, land availability, accessibility, costs, etc. In the bottom-up approach, estimates are based upon starting with disaggregated (state, province or county) estimates that are based on local estimates of productivity, costs, local industry demand, and other constraints which are then aggregated into national estimates. Estimates using the bottom-up approach generally tend to be lower because of the cumulative effect of local constraints. Because the bottom-up approach takes into account local constraints, it may present a more realistic estimate. Additional information from some of the more recent studies is presented below.

Jones et al. (2007) provide an example of inventory-based estimates. These estimates were developed based on literature-based calculations, without economic considerations, and considering optimized use of cropland for energy crops. Their low estimates, for non-crop feedstocks, are based upon using only the feedstock which currently has no other use. Their high estimate, for non-crop feedstocks, assumes that all of the available feedstock will be used to produce fuel. For corn feedstock, their low estimate is based upon maintaining sufficient production of animal and human food, while their high estimate assumes all available crop land is used for growing corn and all the corn is converted to fuel. These estimates ranged from 190 to 3849 mbdmt/yr. They note that while high levels of ethanol production are possible, they may not be socially or ecologically desirable, or may be extremely costly in terms of higher food prices, loss of biodiversity, water degradation, and soil erosion.

The estimates of the supply of feedstocks that can be economically developed are lower than those based on simply feedstock availability. Walsh (2008) estimated the US supply of biomass for 2010 to range from 6 to 256 mbdmt/yr for feedstock costs ranging from \$22 to \$110/bdmt, respectively, and for 2020 to range from 90 to 577 mbdmt/yr for feedstock costs ranging from \$33 to \$110/bdmt. Kumarappan et al. (2009) estimated the metric tons of available cellulosic biomass from MSW, agricultural residue, forest and mill residue, and energy crops that could be economically delivered to a biorefinery for a given price. These results are shown in Table 2-1. The cost at the biorefinery gate includes the cost of producing, harvesting, and transporting the biomass plus a profit for the producers, harvesters, and transporters. The available biomass increases with price due to the incentive to harvest more of the available biomass or to specifically grow energy crops. At a price at or below \$60/bdmt, farmers would not convert any of their food growing land to energy crops because they would get a higher price for their food crops. Note that the quantity supplied approaches Walsh's estimate of 577 mbdmt/yr at a price of \$110/bdmt in 2020.

Table 2-1: Biomass Supply Estimates for the US

<i>Price at biorefinery gate (\$/bdmt)^a</i>	<i>Quantity Supplied, Million bone dry metric tons/yr (mbdmt/yr)</i>				
	MSW	Agricultural Residue	Forest and Mill Residues	Energy Crops ^b	Total ^c
30	15	110	12	0.0	137
40	32	204	80	0.0	315
50	36	234	114	0.0	384
60	58	245	130	0.0	434
70	63	248	133	35	480
80	75	249	135	52	512
90	86	250	135	73	544
100	98	250	135	85	568

^a In 2008 US dollars

^b Assumes a maximum of 10% of crop land in eastern half of US planted with energy crops.

^c Total quantities are different from the summed up values due to rounding.

At a national level, the US Energy and Security Independence Act (EISA 2007) mandates production of 36.0 billion gallons of renewable fuel by 2022. Twenty-one of the 36 billion gallons must be advanced biofuel, and 16 of the 21 must be cellulosic biofuel. The act defines renewable fuel as fuel produced from renewable biomass. It defines advanced biofuel as all renewable fuel, other than ethanol derived from corn starch that has greenhouse gas emissions, as determined by the Administrator, that are at least 50% less than baseline lifecycle GHG emissions. It defines cellulosic biofuel as renewable fuel derived from any cellulose, hemicelluloses, or lignin that has lifecycle greenhouse gas emissions at least 60% less than the baseline lifecycle greenhouse gas emissions. This legislative target provides an important benchmark against which the available biomass feedstock can be evaluated. Some studies related to the feedstock needs to meet the EISA goals are discussed below.

Kumarappan et al (2009) estimated the biomass feedstock requirements needed to meet the ethanol production targets of 7, 14, and 21 billion gallons, assuming a 70 gal ethanol yield per ton of cellulosic feedstock. [The 70 gal ethanol yield per ton is within the theoretical ethanol yields of 56.8 gal/bdt for cotton gin trash to 116.2 gal/bdt for mixed paper range reported by the

AFAVDC (2009a)]. The Kumarappan et al. estimates are shown in Table 2-2. Kumarappan et al. (2009) then estimated the geographical distribution of feedstocks required to meet the EISA mandated 21 billion gallons of advanced biofuel. These results are shown in Table 2-3. Their results indicate that there is adequate biomass available to meet the EISA 2022 mandate. Based upon Table 2-3, California would contribute 0.92 mbd/yr from agricultural residue, and 5.02 mbd/yr from forest and mill residues towards the 2022 US mandated target of 21 billion gals of cellulosic ethanol.

Table 2-2: Biomass Feedstock Requirements and Expected Composition to meet Cellulosic Ethanol Production Targets in the US

Ethanol production target billion gal (at 70 gal/dt)	7	14	21
Required biomass (million dt)	100	200	300
Agricultural Residues	67.3	147.0	180.0
Energy crops	-	-	9.0
Forest and Mill Residues	12.0	22.0	80.0
MSW	20.7	31.0	31.0

Notes: (1) collecting logging residues was found to be uneconomical at prices below \$50/bdmt, (2) energy crops are competitive with field crops in south-eastern states at prices around \$50/bdmt, (3) states near the bottom of Table 2-3 are unlikely to have cellulosic ethanol plants due to the low quantities of biomass available

Several assumptions/estimates were utilized in the Kumarappan et al. (2009) study. It was assumed that 66% of the MSW is organic material suitable for cellulosic ethanol production. Agricultural residues were estimated for four crops – barley, corn, rice, and wheat, respectively, using average residue factors of 1.5, 1, 1, and 1.27, respectively. Forest and mill residues consisted of logging residues generated during harvesting operations, and mill residues generated in saw mills, paper mills, and other harvesting operations. Mill residues were assumed to be available if the price offered is greater than the opportunity cost of their current use as fiber, fuel, or other applications. Switchgrass was chosen as the energy crop. The price of switchgrass compared to the predominant crop in the county, e.g., corn, soybeans, wheat, rice, barley, oats, or cotton, was used to estimate if farmers would switch from a food crop to an energy crop.

The Biomass R&D Technical Advisory Committee is a panel established by the Congress to guide the future direction of federally funded biomass R&D. This panel envisioned a 30 percent replacement of the current U.S. petroleum consumption with biofuels by 2030 (Perlack et al. 2005). They were asked to determine if the land resources of the US can produce a sustainable supply of biomass to displace 30% or more of the country’s current petroleum consumption. They concluded that accomplishing this goal requires ~1 billion dry tons of biomass feedstock per year. They concluded that quantity of biomass could be available by around the middle of the 21st century. The challenge of utilizing this level of biomass would then be developing the infrastructure to collect, process, and convert these feedstock sources economically into Biofuels. Table 2-4 presents a summary of their estimates. Note that in Table 2-4 the estimate for the total biomass availability in 2005 was 483 mbdmt/yr, which is in the same range as the studies discussed above.

Table 2-3: Geographical Composition of Feedstock to meet EISA 2022 Mandate

Biomass supply distribution by state (mbdt/yr) for target biomass quantity of 300 mbd/yr							
State	Agricultural	Energy Crops	Forest	and	Mill	MSW	Total
Minnesota	18.95	-	1.04			0.84	20.83
Nebraska	20.09	-	0.07			-	20.16
Indiana	16.06	-	0.65			-	16.71
Michigan	4.34	-	1.40			4.51	10.25
Washington	2.31	-	5.68			1.94	9.93
Ohio	8.70	-	0.91			-	9.61
Texas	3.21	3.36	2.23			-	8.80
Georgia	0.09	0.66	7.33			-	8.08
Oregon	0.06	-	6.54			0.87	7.47
Wisconsin	5.47	-	1.69			-	7.16
Florida	-	0.09	2.03			4.57	6.69
Idaho	2.18	-	4.42			-	6.60
Alabama	0.01	0.66	5.91			-	6.59
South Dakota	5.92	-	0.15			-	6.07
California	0.92	-	5.02			-	5.94
Missouri	4.63	-	1.11			-	5.73
Pennsylvania	0.08	-	1.49			3.52	5.08
North Carolina	0.18	0.85	4.02			-	5.04
Mississippi	0.39	0.07	4.58			-	5.04
Virginia	0.24	0.17	2.21			2.06	4.68
Louisiana	0.80	0.09	3.61			-	4.50
Kentucky	2.40	0.58	1.49			-	4.46
Arkansas	0.31	-	3.66			-	3.96
Kansas	3.25	-	0.05			-	3.30
Tennessee	0.83	0.58	1.63			-	3.04
South Carolina	-	0.51	2.51			-	3.02
Oklahoma	0.86	1.09	0.66			-	2.60
Montana	0.46	-	1.95			-	2.41
Maryland	0.65	-	0.17			1.36	2.18
New Jersey	-	-	0.08			1.98	2.06
West Virginia	-	0.46	0.82			0.58	1.86
Colorado	1.37	-	0.22			-	1.60
New Hampshire	-	-	0.94			0.39	1.33
New York	0.07	-	1.18			-	1.25
Massachusetts	-	-	0.17			0.98	1.14
North Dakota	1.01	-	0.01			-	1.01
Delaware	0.46	-	0.02			0.35	0.83
Other States	0.13	-	1.40			1.14	2.67
US Total*	180.00	9.00	80.00			31.00	300.00

Table 2-4: Summary of Potential Biomass for different scenarios

Residue source	Biomass available for fuel production (mbdmt/yr) by ~2030				
	(2005) Current	moderate crop yield increase, no land use change	High crop yield increase, no land use change	moderate crop yield increase, land use change	High crop yield increase, land use change
Agriculture	193.7	423.2	597.3	581.3	997.7
Forest and Mill	261.2	325.0	325.0	325.0	325.0
Municipal	28.0	28.0	28.0	28.0	28.0
Total	482.9	776.2	950.3	934.3	1350.7

Perlack et al. utilized a number of assumptions in estimating future availability, including the following:

- Yields of corn, wheat, and other small grains were increased by 25 percent for moderate crop yield increase and 50 percent for high crop yield increase;
- the residue-to-grain ratio for soybeans was increased to 2:1;
- harvest technology was capable of recovering 75 percent of annual crop residues (when removal is sustainable);
- all cropland was managed with no-till methods;
- 55 million acres of cropland, idle cropland, and cropland pasture were dedicated to the production of perennial bioenergy crops for the land use change scenarios;
- all manure in excess of that which can be applied on-farm for soil improvement under anticipated EPA restrictions was used for biofuel; and
- all other available residues were utilized.

Based upon the assumptions in the Perlack et al. (2005) report, the major increase in available biomass by 2030 will be from increases in grain production and dedication of land for the growing of energy crops. Based upon the numbers in Table 2-4, for 2030 in comparison with 2005, the total biomass available will be ~43% higher with moderate crop yield increase and no land use change, while with land use change it will be ~70% higher. The yield increase for agriculture residue by itself for the same moderate crop yield conditions is ~132% and ~225%, respectively. For the high crop yield increase, the percentage increases from 2005 are ~72% and ~140% for total biomass and ~235% and ~471% for agriculture residue alone.

Milbrandt (2005) estimated the inventory of biomass available for each of the 50 US states. Her total estimate is 135 mbdmt/yr less than the Perlack et al. (2005) estimate for the US. If this latter estimate is closer to reality, then the Perlack et al. (2005) estimates may also overestimate the available biomass for 2030. Milbrandt's estimates for the US, from Table 10 of her report, are: agricultural residues – 159.4 mbdmt/yr, forest and mill residues – 136.4 mbdmt/yr, municipal – 43.7 mbdmt/yr, and energy crops – 83.6 mbdmt/yr, for a grand total of 423.1 mbdmt/yr. The agriculture residues include: crop residues and methane from manure management. The forestry and mill residues include: forest residue, primary mill residue, and secondary mill residue. The municipal estimates include: methane from landfills, urban wood, and methane from domestic

wastewater. Switchgrass grown on conservation reserve program (CRP) lands was used for the energy crop. The primary mill residue contributes 77.1 mbdmt/yr to the forest and mill residues. However, based upon Table 4 in Milbrandt's report, 75.5 mbdmt/yr are already being used for other commercially valuable products. Therefore, the total forest and mill residue available for possible fuel production is 60.8 mbdmt/yr. This would reduce the grand total of biomass available for fuel production to 347.5 mbdmt/yr.

2.3 Biomass Availability in California

The most comprehensive estimate for California was made by the California Biomass Collaborative (Williams et al., 2008), a statewide partnership of government, industry, academia, and environmental organizations administered by the University of California, Davis. The Collaborative charter/mission statement indicates: "The Collaborative works to enhance the sustainable management and development of biomass in California for the production of renewable energy, biofuels, and products." In 2008, they updated previous reports assessing biomass resources in California (Williams et al., 2008). They estimated the California gross annual biomass resource in 2007 to be 83 mbdmt/yr and the technically sustainable annual biomass resource in 2007 to be 32.6 mbdmt/yr. The differences between the gross and technically sustainable values account for the fact that not all the available biomass can be used for energy production. For example, not all forestry residues can be harvested, since a certain amount needs to be retained in the land to prevent soil erosion. Another example is that out of the total 36 million dry tons of MSW available each year; only 9.6 million dry tons can be utilized effectively. This estimate takes into consideration Assembly Bill 939 requiring that 50 percent of the MSW collected be recycled or composted back into the earth.

Table 2-5 presents the gross and the technically sustainable source breakdown from the Williams et al. (2008) report for 2007 and for projections to 2010, 2017 and 2020. Of the gross annual resources, 25% (20.6 mbdmt/yr), was from agriculture, 32% (26.8 mbdmt/yr) was from forestry, and 43% (35.6 mbdmt/yr) was from municipal solid waste. Of this technically sustainable resource, 26% (8.6 mbdmt/yr) was from agriculture, 44% (14.3 mbdmt/yr) was from forestry, and 29% (9.6 mbdmt/yr) was from municipal solid waste. The Williams et al. (2008) report was primarily devoted to assessing biomass availability for electrical generation. While they evaluated the availability of landfill gas and waste water treatment, they chose not to include them in Table 2-5, apparently because they are already being used for that purpose.

The estimates by Williams et al. (2008) were higher than those provided by Milbrandt (2005). Milbrandt estimated the total gross biomass available in California to be 13,439 mbdmt/yr, with 1,801 mbdmt/yr from agricultural residues, 6,322 mbdmt/yr from forest and mill residues, 5,316 mbdmt/yr from municipal wastes, and 0 mbdmt/yr from energy crops. Of the forest and mill residues, based upon Milbrandt's Table 4, 4,764 mbdmt/yr of the primary mill residue is already being used for other commercial purposes. Therefore, the total biomass available for fuel production is $13,439 - 4,764 = 8,675$ mbdmt/yr. While Milbrandt (2005) used primarily 2002 data available from the US Department of Agriculture, the Williams et al. (2008) study used more recent data from various California agencies. The Williams et al. (2008) study developed the gross and technical potentials independent of competing uses for the resource, while Milbrandt (2005) considered competing uses. These, plus other assumptions, in the two studies

presumably account for the large differences in the potential biomass estimates. It is also worth noting that the 40.4 mbdmt/yr available for fuel production in 2020 from Williams et al. (2008) study is considerably higher than the 5.94 mbdmt that Kumarappan et al. (2009) estimated California would need to supply to meet the EISA mandate for 2022.

Table 2-5: Gross and technical annual biomass resources (mbdmt/yr) in California, 2007 – 2020

Year	<i>Gross</i>				<i>Technically Available</i>			
	2007	2010	2017	2020	2007	2010	2017	2020
Total Biomass	83.0	88.7	95.4	98.1	32.6	35.7	39.6	40.4
Total Excluding Dedicated Crops	83.0	86.4	90.4	93.1	32.6	33.7	35.1	35.9
Total Thermal Conversion	66.0	70.5	75.6	77.2	26.0	29.1	32.3	32.7
Total Biological Conversion	16.7	18.2	19.8	21.0	6.1	6.7	7.3	7.7
Total Municipal	35.6	37.8	40.0	41.6	9.6	10.3	10.9	11.3
Biosolids landfilled	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Biosolids diverted	0.7	0.7	0.8	0.8	0.6	0.6	0.6	0.7
Total MSW biomass landfilled	18.3	19.4	20.5	21.3	9.1	9.7	10.3	10.7
Total MSW biomass diverted	16.6	17.7	18.7	19.4	0.0	0.0	0.0	0.0
Total Agriculture	20.6	21.9	23.6	24.8	8.6	9.1	9.9	10.3
Total Animal manure	10.2	11.3	12.5	13.4	3.5	3.9	4.3	4.6
Total Cattle manure	8.4	9.4	10.5	11.2	3.1	3.5	3.9	4.1
Total Dairy cow manure	3.9	4.4	5.0	5.3	2.0	2.2	2.5	2.7
Total Orchard and vine	2.5	2.6	3.0	3.1	1.7	1.8	2.1	2.2
Total Field and seed	4.8	4.7	4.7	4.7	2.1	2.0	2.0	2.0
Total Vegetable	1.7	1.7	1.8	1.8	0.1	0.1	0.1	0.2
Total Food processing	1.5	1.5	1.6	1.7	1.2	1.2	1.3	1.4
Total Forestry	26.8	26.8	26.8	26.8	14.3	14.3	14.3	14.3
Total Dedicated crop	0	2.3	5.0	5.0	0.0	2.0	4.5	4.5
Landfill gas	-	-	-	-	-	-	-	-
Waste water treatment	-	-	-	-	-	-	-	-

The University of California at Riverside’s (UCR) College of Engineering – Center for Environmental Research and Technology (CE-CERT) has also made some estimates of the total biomass residue streams available for fuel production in the state of California, with an emphasis on biomass availability in the Southern California area (Norbeck et al., 2008). Table 2-6 shows the inventory from this study for the entire state of California along with details for selected cities and counties in the Southern California region. These estimates were constructed using the data from the Williams et al. (2008) report, augmented by data from the California biomass reporting system by Williams and Gildart (2007), as well as a brief on biomass reported by Moller (2005). The MSW waste stream profiles were obtained from the California Integrated Waste Management Board (CIWM, 2007). Data on the biosolids were compiled through personal correspondences with the public works department in each city/county office. The statewide data is nearly the same as the Williams et al. (2008) data, since data from the Williams et al. report accounts for the bulk of the inventory. The Southern California counties included in this assessment are shown in Figure 2-1.



Figure 2-1: Map of California with County Lines Defining Southern California

The characterization of biosolids was one important element of the CE-CERT study. In addition to the biomass residue streams, 5.6 million dry tons of biosolids are generated annually in the United States (Committee on Toxicants, 2002). The average dry weight per capita of biosolids produced after the primary, secondary and even tertiary treatment steps are approximately 90 g per person per day (Davis, 1996). A total of approximately 0.5 million dry tons per year of biosolids (2-3 million tons of wet biosolids equivalent) are available for use in the state of California. Approximately 0.3 million dry tons of biosolids are produced each year in the Southern California counties included in the CE-CERT study, with much of the biosolids generated are from Los Angeles County, as seen in Table 2-6 (Williams and Gildart, 2007). It is expected that as the population in Southern California continues to increase, both the generation of biosolids, as well as the demand for energy production, will both continue to increase.

In addition to biomass feedstocks, other non-biomass (carbonaceous) municipal waste materials can be used as potential feedstocks for fuel production using processes like gasification. Table 2-7, provides an inventory of non-biomass materials for California and Southern California counties that would be suited for pyrolysis or gasification, but not necessarily other processes. This includes textiles, plastics, and tires. It is estimated an additional 2.9 million dry tons of non-biogenic MSW materials that are landfilled in California each year can be used for energy purposes (CIWM, 1999). Note that the inventory in Table 2-6 for the MSW only includes feedstocks that are considered as biomass, and thus excludes these non-biomass materials.

Table 2-6: California Biomass and Biogenic Municipal Waste Inventory

Units: Dry Tons/Year	Total Biomass Produced in California	Biomass that can be effectively be utilized in California	Southern California	Imperial County	Los Angeles County	Orange County	Riverside County	San Bernardino County	San Diego County	Ventura County
Total Biomass	83,362,000	32,520,590	8,127,655	444,265	2,822,940	1,023,340	1,019,740	1,359,635	1,164,135	293,600
Total Municipal	36,000,000	9,635,590	6,024,405	60,005	2,693,080	1,011,500	622,050	549,265	861,905	226,600
Biosolids Landfilled	123,000	0	0	0	0	0	0	0	0	0
Biosolids Diverted	898,000	558,400	303,700	2,400	170,500	44,000	40,100	27,100	5,200	14,400
Total MSW Biomass Landfilled	18,300,000	9,077,190	5,720,705	57,605	2,522,580	967,500	581,950	522,165	856,705	212,200
Paper/Cardboard	8,000,000	3,993,100	2,480,800	26,400	1,134,950	389,800	239,050	218,100	375,100	97,400
Food	1,900,000	925,500	570,250	6,100	263,000	85,700	55,400	50,550	88,950	22,550
Leaves and Grass	710,000	354,830	250,885	2,345	100,885	32,870	53,400	19,385	33,345	8,655
Other Organics	1,800,000	892,350	523,250	5,900	253,850	82,850	26,700	48,750	83,850	21,750
C&D Lumber	3,800,000	1,784,800	1,099,950	11,800	507,300	185,300	106,850	97,500	187,850	43,550
Prunings, trimmings, branches & stumps	2,258,000	1,128,510	821,025	5,080	262,795	231,180	106,005	87,880	109,810	18,295
Total MSW Biomass Diverted	16,600,000	0	0	0	0	0	0	0	0	0
Total Agricultural	20,562,000	8,615,000	672,650	241,860	4,660	1,740	168,990	170,870	51,730	32,800
Total Animal Manure	10,150,000	3,475,000	474,800	156,800	3,400	300	121,200	185,800	24,800	2,500
Total Cattle Manure	8,380,000	3,077,500	417,900	155,800	3,200	300	93,300	152,800	10,000	2,500
Milk Cow Manure	3,920,000	1,980,000	195,000	6,000	3,200	0	68,500	112,800	4,500	0
Total Orchard and Vine	2,492,000	1,744,000	77,800	2,800	530	40	24,230	2,590	24,780	22,850
Total Field and Seed	4,750,000	2,054,000	88,140	62,900	720	0	17,160	2,080	1,250	2,030
Total Rice Straw	1,700,000	850,000	0	0	0	0	0	0	0	0
Total Vegetable	1,852,000	128,000	30,750	19,580	10	140	6,370	400	920	3,350
Total Food Processing	1,518,000	1,214,000	3,580	0	0	1,260	30	0	0	2,270
Total Forestry	26,800,000	14,270,000	1,430,600	142,400	125,200	10,100	228,700	639,500	250,500	34,200
Mill Residue	8,200,000	3,330,000	35,700	0	5,900	200	2,800	17,000	5,800	4,200
Forest Thinnings	7,700,000	4,110,000	18,900	0	500	0	500	3,700	14,200	0
Logging Slash	8,000,000	4,250,000	109,000	0	18,000	1,200	6,000	42,300	28,800	14,900
Chaparral	4,900,000	2,580,000	1,287,000	142,400	102,800	8,700	219,400	578,500	202,100	15,100

Table 2-7: Non-Biomass Material from Municipal Waste Inventory for Selected California Counties

Units: Dry Tons/Year	Total Non-biomass materials Produced in California	Non-biomass that can be effectively be utilized in California	Southern California	Imperial County	Los Angeles County	Orange County	Riverside County	San Bernardino County	San Diego County	Ventura County
Other MSW Materials Landfilled	5,826,633	2,913,317	2,378,504	15,327	1,157,470	467,473	147,485	169,087	337,916	83,745
Plastic	4,100,000	2,050,000	1,787,301	12,252	911,393	284,668	116,026	132,867	263,999	66,077
Textiles	1,600,000	800,000	537,094	2,735	219,556	174,407	27,473	31,744	66,527	15,652
Tires	126,633	63,317	54,109	340	26,522	8,398	3,986	4,456	8,390	2,017

Of the approximately 8.1 million dry tons of the biomass and municipal wastes generated in Southern California as potential feedstocks for alternative fuel production, most of this amount is MSW, with smaller contributions from Ag and forestry residues. The total amount of biogenic MSW that can be effectively utilized for energy purposes in Southern California is 5.7 million dry tons per year. The largest component of landfilled biogenic MSW in Southern California is paper and cardboard (2.5 million dry tons per year), with much of this generated from Los Angeles County. Green waste (prunings, trimmings, branches, and stumps) and construction and demolition lumber (C&D) combined represent a potential amount of close to 2 million dry tons per year in Southern California. The green waste and C&D lumber in MSW also contributes to wood waste because it consists of a mixture of woody and herbaceous materials such as wood chips, logs, stumps, tree tops, and brush (McKeever, 2004).

The amount of agricultural residues that is available in Southern California for energy purposes is 0.7 million dry tons per year. Most of the agricultural residues generated in Southern California consist of animal manure, specifically in Imperial, Riverside, and San Bernardino counties, where, approximately 0.5 million dry tons per year are produced. In addition, there is potential for 1.4 million dry tons per year of forestry residues to be effectively utilized in Southern California. This is low in comparison to the rest of the state because the forests residues are concentrated in northern California, as illustrated in Figure 2-2 (Kadam et al., 1999). The primary constituent of forestry residues in Southern California is chaparral, which accounts for 1.3 million dry tons per year. Chaparral is a type of shrubbery (ever-green plant) which grows well in arid climates such as Southern California and is considered a type of woody biomass.

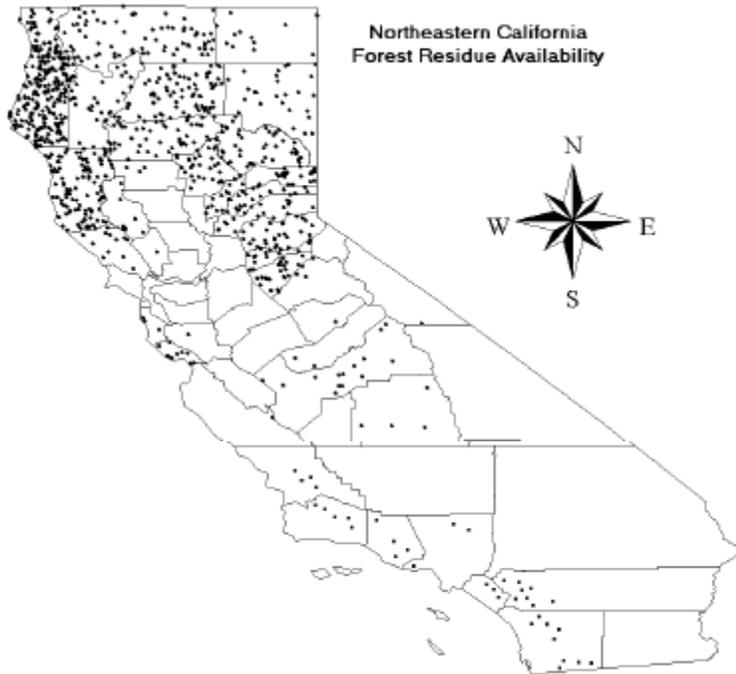


Figure 2-2: Forest Biomass Potential in California

2.4 Accessibility, Collection, Harvesting, and Transportation of Biomass

Other important issues with the use of biomass for fuel production is its accessibility and how readily this biomass can be collected/harvested and transported. A feedstock must also be available in considerable quantities in specific locations to make it advantageous for use in fuel production. For example, in California, chaparral is available in large quantities, but it is not concentrated in specific locations. The majority of the current literature that calculates the costs for transporting biomass to a biomass conversion facility uses a distance of 50 miles or less of one way transport of biomass to an energy conversion plant (Gray et al. 2007, Ghafoori 2007, Searcy & Flynn 2010, and Huang et al. 2009), so this is a good measure of the density of biomass that would be needed at a specific location. Related to accessibility, is the issue of seasonal variation and the degree to which a feedstock can be continuously supplied throughout the year.

UCR's CE-CERT has evaluated some different scenarios for transportation costs within the Southern California area (Jermisirisakpong et al., 2010). As part of this study, ArcGIS was used to depict different scenarios of transporting biomass feedstock to a desired energy conversion facility that would be located in Southern California. Scenarios were performed for transportation of biomass from both active landfills and waste water treatment plants to a conversion facility, with the CE-CERT hydrogasification process being used as the technology for the conversion facility. The baseline cost estimate from this model was \$4.59 per ton to transport biomass. This cost was based on a 50 mile transport radius, a truck capacity of 10 tons, a fuel price of \$2.41, a fuel economy of 5 miles per gallon, and a moisture content of 6%. The CE-CERT Transportation Cost Model is also applicable to other types of energy conversion facilities that require the hauling of biomass. Additionally, the CE-CERT model considers

several other factors that other models do not take into account, such as allowing for co-mingled feedstock when appropriate.

2.5 Biomass Fuel Potential

It is important to understand the fuel volume that can be generated from a given amount of biomass relative to consumption in order to understand how much fuel that resource will be able to displace. The average gasoline usage for the US in 2008 was 137,801,000,000 gallons (Energy Information Administration, 2009). The average annual gasoline consumption in California from 2002 to 2007 was 15,584,000,000 gallons (EIA, 2009). Assuming that the yield of ethanol per ton of biomass is independent of the nature of the biomass, and is equal to 70 gallons ethanol/ton biomass, then the annual potential ethanol yield for the estimated tons of biomass reviewed in this chapter are shown in Table 2-8, on a volumetric basis. Based upon the total US consumption of gasoline in 2008, if all the estimated biomass for 2005 were processed to produce ethanol it could have replaced ~18 to ~25% of the gasoline. For comparison, the amount of ethanol currently being produced from corn-based ethanol production was 8% of the total gasoline use in the country. For the same assumptions, if all ethanol for use in California were produced from California biomass, then ~4% to ~15% of the California gasoline could have been replaced in the 2005 to 2007 time frame. All of the above percentages are upper limits because ethanol has lower energy content than gasoline, so it takes a larger volume of it to move a vehicle the same distance as gasoline. Based upon the energy content of gasoline (~124,000 Btu/gal) and ethanol (~82,000 Btu/gal) it would take ~1.5 gallons of ethanol for a vehicle to travel the same distance it can travel on 1 gallon of gasoline. Therefore, the minimum and maximum potential % of gasoline that could have been replaced in the 2005 to 2007 timeframe on an energy basis would range from ~3 to 10% for California and ~12 to 16% for the US. Since some of the studies reviewed predict that greater quantities of biomass will be available in future, it is possible that greater percentages of gasoline could be displaced with these higher volumes. By 2030, if the amount of gasoline which would be consumed has not increased, then the potential ethanol could replace ~69% of the gasoline. By 2020, California can potentially produce enough ethanol from California biomass to replace ~18% of the California gasoline.

Table 2-8: Potential Ethanol from Estimated Biomass (Assumes 70 gal ethanol/ton biomass)

Estimated Biomass (mbdt/yr)		Year	Potential Ethanol (bgal/yr)		% of gasoline use		Reference
US	Calif		US	Calif	US	Calif	
-	32.6	2007	-	2.282		14.64	California Biomass Collaborative 2008
-	35.7	2010	-	2.499			
-	39.6	2017	-	2.772			
-	40.4	2020	-	2.828			
347.5	8.68	2005	24.325	0.6076	17.65	3.90	Milbrandt 2005
482.9	-	2005	33.804	-	24.53		Perlack et al. 2005
776.2	-	2030	54.335	-			
950.3	-	2030	66.522	-			
934.3	-	2030	65.402	-			
1350.7	-	2030	94.550	-			
		Annual gasoline usage (bgal/yr) = 15,584.0					Californian Board of Equalization 2009
		Annual gasoline usage (bgal/yr) = 137,801.37					Energy Information Administration 2009

2.6 Natural Gas Availability

Natural gas is typically produced along with crude oil or from deep natural gas wells, making it a non-renewable fossil fuel. In the early 1990's, it was thought that natural gas production had peaked and would decline in the coming decades. This has not been the case, however, because technology has been developed to release the gas from tight shale formations. Navigant Consulting (2008) prepared a report for the American Clean Skies Foundation assessing the supply of natural gas in North America. There are at least 21 major US Shale Basins located in over 20 states. The major source of increased natural gas production has come from seven of these basins. The seven basins that have been the major source to date are located in Texas, Oklahoma, and states east of the Mississippi River. California obtains 13.5% of its NG from in-state sources, 23.4% from Canada, 27.7% from the Rockies, and 40.3% from the southwest. Navigant estimates that the total domestic proven reserves plus the ultimately recoverable domestic resource base is in the range of 1,680 to 2,247 Tcf. At current production levels, this is enough gas for 88 to 117 years. California used 6,316 million cubic feet of NG per day in 2006.

2.7 Biomethane Availability

Biomass can provide a renewable source of natural gas. Anaerobic digestion of organic waste material produces methane, the principal component in natural gas, which is commonly called Biomethane. Organic waste includes manure, crop residues, food processing waste, slaughterhouse waste, rendering plant wastewater, and green waste from municipal/commercial collection programs.

Krich et al. (2005) estimated the annual potential production of Biomethane from the anaerobic digestion of various waste products in California. They estimate the total gross potential is about 124 billion ft³ CH₄/yr (BCF/yr), but that due to inefficiencies in collection, contamination with other wastes, and other uses, the technical potential (i.e., the amount that can be realistically collected and used) is 23 BCF/yr. Krich et al. were primarily interested in the production of biomethane from dairy wastes and wastes that could be co-digested with dairy wastes. Over half of the total gross potential of 124 BCF/yr is from processed green waste and landfills that cannot be co-digested with dairy manure. Dairy manures represent about 2/3 of the technical potential 23 BCF/yr. Currently, most dairy manure is stored in large lagoons under aerobic conditions. Under these conditions, the methanogenic bacteria that digest the manure release methane into the atmosphere.

Williams et al. (2008) states that potential landfill gas production in California exceeds 118 BCF/yr, with a potential recovery of 79 BCF/yr. In 2003, there were 330 active landfills in California and 217 landfills had existing or potential landfill gas to energy recovery (See Table 3.4.1 in Williams et al. [2008]). Currently, this recovered biomethane is primarily used to generate electricity or heat. The report also states that biogas from waste treatment plants adds 16 – 18 BCF/yr. The total statewide demand for all uses of natural gas is about 2,200 BCF/yr, so the potential of biomethane from wastes is ~1% of the total demand.

2.8 Coal Reserves

Coal is the most widely distributed fossil fuel around the world. While coal would not likely be suitable for meeting California's long-term alternative fuel needs, since it is non-renewable and environmentally destructive to harvest or mine, these estimates are included for completeness. British Petroleum estimated at the end of 2008 that there were 826,001 million tons of *proven* coal reserves worldwide, or 122 years of coal available at current production rates (British Petroleum 2009). A breakdown of these reserves is provided in Table 2-9 by country.

The US has the largest recoverable share of coal in the world, with over 27% of the total coal reserves. Slightly over half of the reserves are subbituminous or lignite, which would be the most appropriate for use in gasification. The 238 gigatons of coal reserves in the US represent the energy equivalent of approximately 1,055 billion barrels of oil. While this is significantly more than the other biomass feedstocks discussed throughout this report, it must be noted that a large fraction of coal use is typically for electrical power generation in the US. From a usability standpoint, bituminous and anthracite have the highest energy content and are best for electricity generation, while subbituminous and lignite are more volatile and more suited for thermochemical processes, such as gasification or pyrolysis. A breakdown of the coal regions within the US is provided in Figure 2-3. This figure shows that this coal is largely found in areas in the mid-west, south, east, and Rocky Mountains, as opposed to California.

Table 2-9: Proved recoverable coal reserves at end-2008 (million tonnes (teragrams))

Million tonnes	Anthracite and bituminous	Sub-bituminous and lignite	Total	Share of total	R/P ratio
US	106950	129358	238308	28.9%	224
Canada	3471	3107	6578	0.8%	97
Mexico	860	351	1211	0.1%	106
Total North America	113281	132816	246097	29.8%	216
Brazil	-	7059	7059	0.9%	*
Colombia	6434	380	6814	0.8%	93
Venezuela	479	-	479	0.1%	74
Other S. & Cent. America	51	603	654	0.1%	*
Total S. & Cent. America	6964	8042	15006	1.8%	172
Bulgaria	5	1991	1996	0.2%	70
Czech Republic	1673	2828	4501	0.5%	75
Germany	152	6556	6708	0.8%	35
Greece	-	3900	3900	0.5%	58
Hungary	199	3103	3302	0.4%	351
Kazakhstan	28170	3130	31300	3.8%	273
Poland	6012	1490	7502	0.9%	52
Romania	12	410	422	0.1%	12
Russian Federation	49088	107922	157010	19.0%	481
Spain	200	330	530	0.1%	32
Turkey	-	1814	1814	0.2%	21
Ukraine	15351	18522	33873	4.1%	438
United Kingdom	155	-	155	*	9
Other Europe & Eurasia	1025	18208	19233	2.3%	268
Total Europe & Eurasia	102042	170204	272246	33.0%	218
South Africa	30408	-	30408	3.7%	121
Zimbabwe	502	-	502	0.1%	287
Other Africa	929	174	1103	0.1%	*
Middle East	1386	-	1386	0.2%	*
Total Middle East & Africa	33225	174	33399	4.0%	131
Australia	36800	39400	76200	9.2%	190
China	62200	52300	114500	13.9%	41
India	54000	4600	58600	7.1%	114
Indonesia	1721	2607	4328	0.5%	19
Japan	355	-	355	*	289
New Zealand	33	538	571	0.1%	111
North Korea	300	300	600	0.1%	17
Pakistan	1	2069	2070	0.3%	496
South Korea	133	-	133	*	48
Thailand	-	1354	1354	0.2%	75
Vietnam	150	-	150	*	4
Other Asia Pacific	115	276	391	*	26
Total Asia Pacific	155809	103444	259253	31.4%	64
Total World	411321	414680	826001	100.0%	122
of which: European Union	8427	21143	29570	3.6%	51
OECD	159012	193083	352095	42.6%	164
Former Soviet Union	93609	132386	225995	27.4%	433
Other EMEs	158700	89211	247911	30.0%	60

*More than 500 years.

Source of reserves data: World Energy Council, 2009.

*Less than 0.05%.

Notes: Proved reserves of coal – Generally taken to be those quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known deposits under existing economic and operating conditions.

Reserves-to-production (R/P) ratio – If the reserves remaining at the end of the year are divided by the production in that year, the result is the length of time that those remaining reserves would last if production were to continue at that rate.

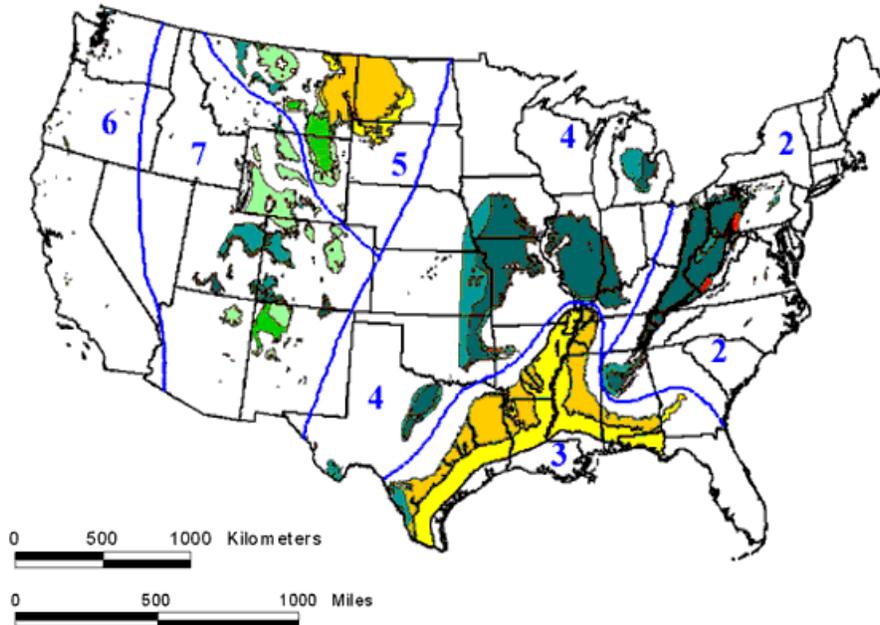


Figure 2-3: Continental United States coal regions

2.9 Methane Hydrates Reserves

Methane hydrates, a clathrate compound, are cage-like lattices of ice crystalline solids inside of which are physically trapped molecules of methane. It is estimated that the amount of carbon stored in methane hydrates is about 10,000 gigatons globally, which exceeds the combined amount of carbon in all known fossil fuels (Desa, 2001). With natural gas providing about 23% of the energy consumed in the US, methane hydrates can be a potential energy source to meet the increasing demand of energy. Generally, two types of methane hydrates deposits exist: those found under Arctic permafrost, where methane hydrates are generated by bacterial activity in the shallow sediments, and those found beneath the ocean floor, where water is more than 500 ft deep and methane hydrates are formed by geological processes.

The potential renewability of methane hydrates has been examined by some researchers. Since methane hydrates can be formed from biogenic as well as thermogenic sources, the amount of time required to regenerate the methane hydrates is an important factor in evaluating renewability. Nimblett and Ruppel (2003) found that a regeneration time of $\sim 10^5$ years was required to produce hydrate concentrations of 10–15% of porosity in a natural system characterized by physical parameters that describe the Blake Ridge, a deep area of the Atlantic Ocean that runs along the east coast of the US. Somewhat shorter regeneration times were predicted for marine hydrate provinces with more rapid fluid flux and methane supply or with significant production of methane under conditions suitable for methane hydrate formation. Overall, it appears that methane hydrate systems cannot regenerate gas hydrate quickly enough for these deposits to be considered a renewable resource.

3 Conventional Alcohols

3.1 Introduction

Currently, ethanol production via fermentation is the most widely produced biofuel in the world. Conventional ethanol production processes are based on the fermentation of sugars through the utilization of yeast and enzymes. The production of ethanol from conventional fermentation processes is a very well developed technology, with a large number of commercial facilities in operation. As shown in Table 3-1, the vast majority of the global production capacity is located in the United States and Brazil. In this chapter, the technical development and ongoing research for conventional alcohol as a transportation fuel are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and research roadmap funding recommendations for conventional alcohols are provided.

Table 3-1: 2009 World Fuel Ethanol Production.

Country/Region	2009 Production (Million Gallons)
United States	10,600
Brazil	6577.89
European Union (EU)	1039.52
China	541.55
Canada	290.59
Other	247.27
India	91.67
Columbia	83.21
Australia	56.80

Source: Renewable Fuels Association, F. O. Licht 2009 Estimates. Presented in “2010 Ethanol Industry Outlook”, Accessed online at http://www.ethanolrfa.org/page/-/objects/pdf/outlook/RFAoutlook2010_fin.pdf?nocdn=1

3.2 Development of Conventional Alcohols for Transportation Fuels

3.2.1 *Feedstocks*

Ethanol may be produced from a variety of biomass feedstocks. Starch-based crops, such as barley, corn, rye, sorghum (milo) and wheat, may be processed to produce ethanol. In the United States, ethanol is typically produced from corn. In Canada and the European Union (EU), starch-based ethanol is typically produced from wheat. Ethanol may also be produced from biomass which has a naturally high concentration of sugar, such as sugarcane and sugar beets. In Brazil, nearly all of the ethanol is produced from sugarcane. These feedstocks all have limitations in terms of availability and potential competition with food production. These issues are discussed in greater detail in section 3.3.

3.2.2 *Production*

The processes for both starch-based and sugar-based ethanol production are commercially proven processes and in widespread use throughout the US and Brazil. There are two

predominant types of processes currently employed in the United States for corn-based ethanol production: wet mill processes and dry mill processes. In the past 10 years, nearly all new ethanol facilities have utilized dry mill technology. In the wet mill process, the corn kernels are first “steeped” by soaking in a mixture of water and SO₂ and then separated into their basic components, i.e., starch, protein, germ, and fiber. These components are then processed to produce corn oil, corn gluten, corn syrups, and ethanol. The dry mill process produces just two main coproducts, ethanol and distiller co-products. The dry mill process begins by grinding the entire corn kernel into flour. The flour is combined with water and processed with enzymes to convert the starch into fermentable sugars (saccharification). Yeast is added to convert the sugars into ethanol and other alcohols (fermentation). Following distillation, the pure ethanol stream is denatured with a small amount of gasoline or other chemicals for tax purposes and to deter human consumption. Schematics for both the wet mill and dry mill processes are provided in Appendix A. The process for sugarcane is simpler than for corn since the sugars can be released from the sugarcane by pressing it, and the enzyme fermentation of sugar to ethanol is easier than the enzyme fermentation of starch to ethanol.

3.2.2.1 Starch-Based Ethanol Production

The ethanol industry in the United States, based largely on starch-based ethanol production methods, expanded rapidly in the past decade, prior to the recent economic downturn. This rapid growth, illustrated in Figure 3-1, was spurred by increasing gasoline prices and production incentives from both federal and state governments. Expansion was further motivated by the enactment of the Energy Policy Act of 2005, which established the Renewable Fuel Standard (RFS). The original RFS mandated that annual renewable fuel production in the United States increase to 7.5 billion gallons by 2012. In 2007, the RFS was amended, increasing the production levels required throughout the period from 2008 through 2022. Due to these factors, many new ethanol plants were built, and the U. S. production capacity expanded from 3.66 billion gallons to 12.7 billion gallons from January 2005 through July 2009, which is about a 250% increase.

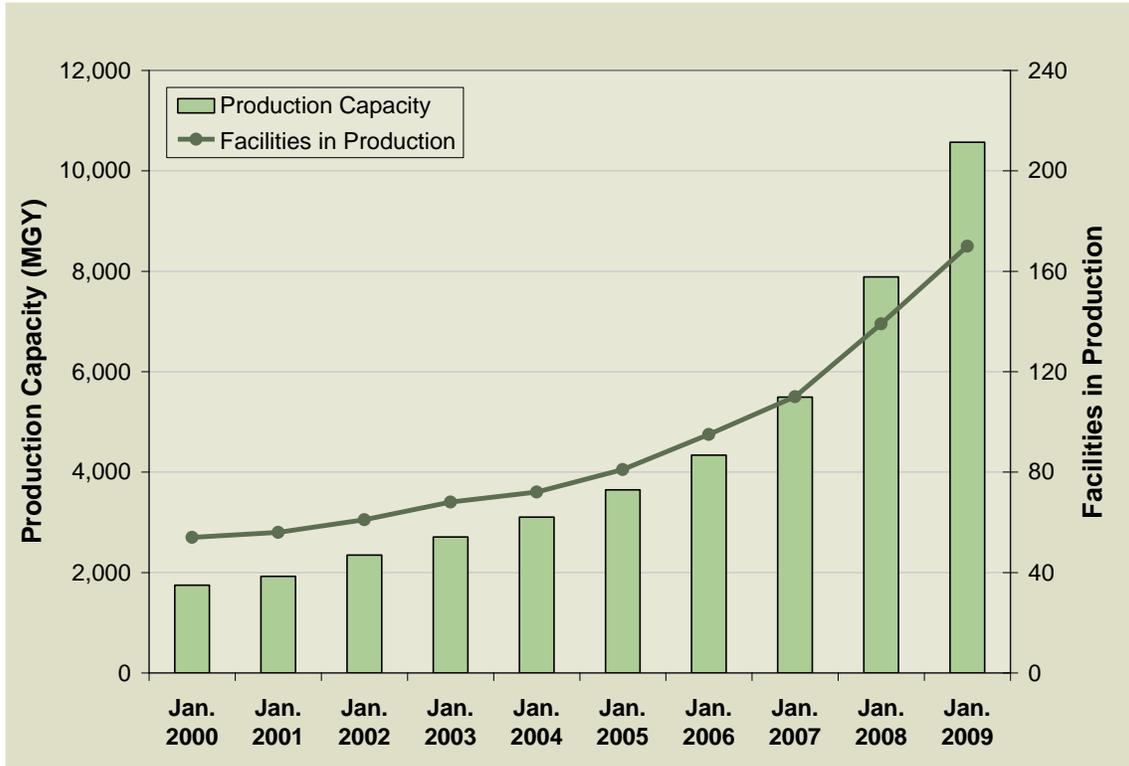


Figure 3-1: Expansion of U.S. Ethanol Industry since 2000 (Renewable Fuels Association).

In 2008 and 2009, significant market pressures curbed the expansion of the ethanol industry. Lower gasoline prices, high corn prices and a tightened credit market during this period contributed to economic difficulties for ethanol producers. As of December 2009, many production facilities are currently idle, and several ethanol producers have declared bankruptcy in the past 24 months (EPM, 2009). According to information provided by the Renewable Fuels Association (RFA, 2010), as of January 2010 there were approximately 200 ethanol production facilities installed in the United States, ranging in nameplate production capacity from less than 1 MGY to 130 MGY. Of these facilities, slightly more than 150 facilities have nameplate ethanol production capacities of greater than 40 MGY. The collective nameplate capacity of ethanol production facilities installed in the United States exceeded 13,000 MGY, with operating production greater than 11,800 MGY (RFA, 2010). The majority of the ethanol facilities are located in the central United States, as shown in Table 3-2.

Table 3-2: Top 10 Ethanol-Producing States as of January 2010*.

State	Nameplate Capacity (MGY)	Operating Production (MGY)	Under Construction/Expansion (MGY)	Total Future Capacity** (MGY)
Iowa	3,293.2	3183.0	380	3673.0
Nebraska	1,523.0	1,454.0	275.0	1,798.0
Illinois	1,350	1,350.0	93.0	1,443.0
Minnesota	1,136.6	1,112.6	0	1,136.6
South Dakota	1,016.0	1,016.0	33	1,049.0
Indiana	908.0	706.0	88	996.0
Ohio	538.0	314.0	0	538.0
Kansas	491.5	436.5	20	511.5
Wisconsin	498.0	498.0	0	498.0
North Dakota	353.0	343.0	0	353.0

Renewable Fuels Association, January 2010.

*Total future capacity is the sum of current nameplate capacity and projected construction/expansion capacity as of January 2010

The leading ethanol producers in the US, as of January 2010, are:

- **POET, LLC (formerly Broin):** 25 plants with a total nameplate capacity of 1,526 MGY.
- **Archer Daniels Midland Co. (ADM):** 7 plants with a total nameplate capacity of 1,070 MGY.
- **Valero Renewable Fuels, LLC:** 10 plants with a total nameplate capacity of 1100 MGY. Valero, a major US petroleum refiner, purchased the assets of now bankrupt VeraSun in 2009.

The total reported ethanol production capacity of these three producers exceeds 3,600 MGY and represents nearly 30 percent of the total ethanol production capacity in the United States. Many other ethanol producers in the United States operate two or less individual facilities with total nameplate production capacities of less than 200 MGY.

The majority of the fuel ethanol for California is transported by rail from the Midwest where the corn is grown and processed into ethanol. The Renewable Fuels Association (RFA, 2010) reported that there are four corn-based ethanol production facilities in California, as of January 2010, with a combined nameplate production capacity of 186.5 million gallons per year (mgy), see Table 3-3, but only 31.5 mgy were in operating production, as Pacific Ethanol was in bankruptcy and had closed its 40 mgy Madera plant and its 60 mgy Stockton plant, and Calgren Renewable Fuels, LLC had not started production at its Pixley plant. More recently, Pacific Ethanol has indicated that it plans to reopen its Stockton, CA facility in December 2010, with additional plans to reopen the Madera facility at a later point (Pacific Ethanol, 2010). The RFA also reported that Cilion had planned to construct a 50 mgy ethanol from corn plant in Keyes, CA. The plant was initially planned to be operational in 2008. Kern county approved the project, but the California Attorney General concluded that they did not properly consider the effect of

CO₂ on global warming. The plant itself is expected to emit 179,000 metric tons of CO₂/yr, plus there will be additional CO₂ from the trains bringing the corn in from the Midwest and the trucks hauling the ethanol to market. The Attorney General and Cilion came to an agreement whereby if Cilion constructs the plant they will have to contract with a tree planting organization to purchase and plant 2,000 trees at \$50/tree over the next five years (California Attorney General, 2009). In addition, they must pay \$390,000 to a fund for the mitigation of greenhouse gases. The majority of the corn processed by these facilities is transported by rail from the Midwest. The Golden Cheese Company of California also has a 5 mgy cheese-based production facility in Corona, CA. The current ethanol operating production capacity in California produces enough ethanol to treat the annual California gasoline demand to a level of only 0.2% ethanol.

Table 3-3: Corn-based ethanol production facilities in California.

Company	Location	Nameplate Capacity (mgy)	Operating Production (mgy)
AltraBiofuels Phoenix Bio Industries, LLC	Goshen	31.5	31.5
Calgren Renewable Fuels, LLC	Pixley	55	0
Pacific Ethanol, Inc.	Madera	40	0
Pacific Ethanol, Inc.	Stockton	60	0

3.2.2.2 Sugar-Based Ethanol Production

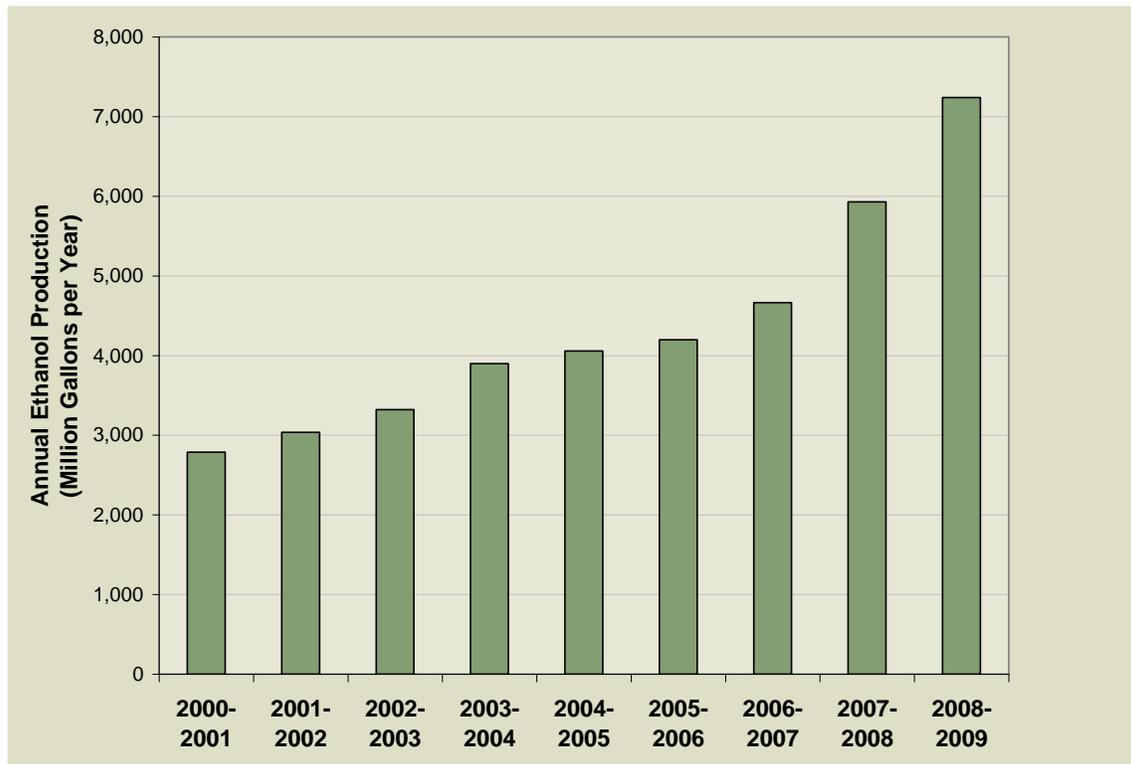
There is general agreement that ethanol production from sugarcane has several advantages over production from corn. The advantages include: (1) a higher ethanol productivity per hectare of land use, (2) less energy to process, (3) greater GHG emission reduction, (4) lower full life-cycle carbon intensity, (5) shorter payback time for GHG emissions, and (6) lower cost of production (Budny and Sotero, 2007; Goettemoeller and Goettemoeller, 2007; Duailibi, 2008; Tachinardi, 2008; Rother, 2006; Macedo et al., 2004; World Bank, 2008; Searchinger et al., 2008; CARB, 2009a; CARB, 2003; Oxfam, 2008; Jalonick, 2008; GADA, 2008). While these advantages can readily be realized in Brazil, where there is an abundance of land that can be used to grow ethanol, these advantages are offset by the more limited area for growing sugarcane in the US, as discussed below. Some additional disadvantages to sugar-based feedstocks, in comparison with starch-based feedstocks, are that sugar-based ethanol feedstocks take much more water to grow, as discussed below, and the crops take about twice as long to reach maturity.

Production of ethanol from sugar-based feedstocks (i.e., sugarcane or sugar beets) is less energy intensive than production from starch-based feedstocks. Rather than the more energy intensive process of grinding the entire corn kernel into flour and employing enzymes to convert starch into fermentable sugars, sugarcane can simply be pressed to efficiently yield fermentable sugars. The remaining fermentation and distillation steps of the process are similar, if not identical, for both the starch- and sugar-based processes.

In addition to the lower energy inputs for sugar-based ethanol methods, facilities that process sugarcane to produce ethanol can also utilize bagasse, the fibrous residues of the sugarcane following pressing. This bagasse may be used as a boiler fuel to provide the process heat and electricity required by the facility, significantly reducing the need to consume fossil fuels in the

ethanol production process. Therefore, the energy balance for sugarcane-based ethanol is significantly better than that of starch-based ethanol. The sugarcane ethanol energy balance estimates (i.e., the ratio of energy value of the fuel produced to the total energy inputs to the process) range from 8.2 to 10.0, while similar estimates for corn-based ethanol average roughly 1.3.

In Brazil, there are more than 300 facilities producing ethanol from sugarcane. A typical sugarcane ethanol facility in Brazil crushes 2 million tons of sugarcane per year to produce 200 million liters of ethanol per year (or, roughly 50 MGY) (Goldemberg 2008). Total ethanol production in Brazil has grown since 2000, as presented in Figure 3-2.



Source: UNICA. Available at: <http://english.unica.com.br/dadosCotacao/estatistica/>.

Figure 3-2: Ethanol Production in Brazil since 2000

As Figure 3-2 illustrates, the sugarcane ethanol industry in Brazil has been significantly expanding. The Brazilian government has recently identified areas of the country where sugarcane production will be precluded. The acreage that remains available for sugarcane production greatly exceeds the acreage currently used by the sugarcane industry, however, according to the Brazilian government (Bevill, 2009). Therefore, it does not appear that these regulations will limit the currently planned expansion of the industry in Brazil.

Efforts to develop sugar-based ethanol facilities in the United States are underway. Because of the limited areas suitable for the growth of sugarcane crops and the relatively high cost of sugar production in the United States, the economics of sugarcane-to-ethanol processes are not as

favorable in the U.S. as they are in Brazil. However, at least two companies are pursuing projects that will produce both ethanol and renewable electricity (Voegelé, 2009). These companies believe that the combination of these revenue streams will provide sufficient returns on investments. These companies are:

- **California Ethanol + Power, LLC:** California Ethanol + Power is the furthest along with plans (California Ethanol and Power, 2009). They have some farmers growing sugarcane but have not started construction of their proposed 60 mgy processing facility at this time. They anticipate that their facility will provide roughly 50 MW of renewable electricity to the grid. The company announced groundbreaking for their first plant, located a few miles southwest of Brawley, CA, in early 2010, with the facility expected to begin operation in the second quarter of 2012.
- **Pacific West Energy LLC:** Pacific West Energy intends to construct a 12 MGY facility on the Hawaiian island of Kauai. The facility will be located at the site of an existing sugar mill and will have the ability to refine sugar or produce ethanol, depending upon market conditions. Pacific West expects the facility to be online by the end of 2010.

While other niche applications of the technology may be viable, it does not appear that sugar-based ethanol facilities are likely to significantly displace existing starch-based ethanol processes in the United States. A combination of the appropriate climate, high value for products, and strong economic (Hawaii) or policy (California) drivers are needed.

3.2.2.3 Biobutanol

Butanol is a 4 carbon alcohol that can also be used as an alternative transportation fuel. Biobutanol has higher energy content than ethanol, and it has fewer issues with water when blended in gasoline. Butanol's primary use is currently as an industrial solvent in products such as lacquers and enamels. Butanol can be produced from biomass or fossil fuels and it can be produced by either fermentation or petrochemical processes. Butanol made from biomass feedstocks is called biobutanol. The biomass feedstocks used for butanol production via fermentation are similar to those used for ethanol fermentation.

One of the primary pathways being considered by biobutanol production is fermentation (Ramey and Yang, 2004; Voegelé, 2009; Butamax Advanced Biofuels LLC, 2009; Cobalt Biofuels, 2008). Louis Pasteur was the first to observe that butanol could be produced by bacterial fermentation in 1861 (Ezeji et al., 2004). Later in 1916, Chaim Weizmann's developed a fermentation process capable of producing a mixture of acetone, butanol, and ethanol. This process was industrialized during WWI, when acetone, required to produce cordite for munitions, came into short supply. This process is more expensive than conventional petroleum processes, however, and hence nearly all of the current butanol production is done via petroleum processes. With the expansion of the petrochemical industry in the 1950s and 1960s, most of the butanol fermentation plants were closed.

The acetone-butanol-ethanol (ABE) fermentation process utilizes bacterial fermentation to produce acetone, butanol, and ethanol from starch. In this process, butyric, propionic, and acetic

acids are first produced by *Clostridium acetobutylicum* in a batch reactor. The culture then undergoes a metabolic shift to form acetone, butanol, and ethanol. The difference from ethanol production is primarily in the fermentation process and minor changes in the distillation process. Existing ethanol plants can be modified to produce butanol, which is a lower capital cost investment than building a plant from the ground up. The production of high titers of butanol via the ABE process is limited, however, because the accumulation of butanol in fermentation broth, even at fairly low titers, exhibits strong toxicity toward microorganisms (Conner and Liao, 2009). The butanol yields from the conventional ABE fermentation process from glucose are typically around ~15% (w/w) and rarely higher than 25% (corresponding to 0.77–1.3 gallons per bushel corn, respectfully) (Ramey and Yang, 2004). Also, if all ethanol plants were converted to biobutanol plants slightly more gasoline might be replaced, due to butanol's higher energy content, but it would not be significant relative to the US demand for gasoline.

Several small scale biobutanol production companies have been launched in recent years. DuPont and BP have been evaluating the potential of biobutanol as a next generation biofuel (Dupont, BP, 2009, AFAVDC, 2009b). In 2007, DuPont and BP worked with British Sugar to convert the United Kingdom's first ethanol fermentation facility to produce approximately 30,000 tons of biobutanol annually. In United States, several venture companies, including GEVO (Voegele, 2009), Butamax (Butamax Advanced Biofuels LLC, 2009), Cobalt Biofuels, and ButylFuel, LLC, have been developing new biobutanol production processes. BP and Dupont commenced their butanol commercialization venture, Butamax Advanced Biofuels, to develop a biobutanol production process from many different types of feedstocks. ButylFuel has developed a process they suggest could make fermentation-derived butanol more economically viable and competitive with current petrochemical processes (AFAVDC, 2009b). This work was done with assistance under a U.S. DOE Small Business Technology Transfer grant. CobaltBiofuels, a California-based venture, opened its butanol production pilot plant in 2010. Cobalt has made advancements in cutting down the cost of biobutanol production using a range of regional, low-cost plant materials to manage feedstock expenses through microbe development, fermentation management, and separation technologies. Another company, GEVO, provides retrofits to existing ethanol plants to make biobutanol from grain crops, sugar cane and sugar beets using its Integrated Fermentation Technology. The status of various domestic and international biobutanol companies is summarized in Table 3-4 and Table 3-5, respectively (Nejame, 2010). Some companies produce n-butanol, while other companies are making isobutanol as alternative fuel. Both n-butanol and isobutanol have good fuel properties and their oxidation rates are very similar. Isobutanol has a higher octane number of 103.5, compared to n-butanol's octane number of 87 (Nejame, 2010).

Table 3-4. Domestic Butanol Company Status

Company	Bug	Bug Strategy	Molecule	Fermentation Process	Separation Strategy	Development Status
Gevo	Yeast	GMO UCLA Valine metabolism	iso-buoh	Semi batch	vacuum flash in situ removal followed by distillation trains	2010 Operating pilot in St. Johns, MO. 2011 Commercial
Cobalt Biofuels	Clostridium	Non GMO strain for reduced etoh and acetone	n-buoh for blending w/gasoline, diesel, jet	Continuous modified ABE Fermentation	vapor compression distillation	2010 pilot 10-35k gpy 2011 demo 2-5m gpy 2012 commercial
Tetra Vitae	Clostridium beijerinckii	Non GMO selected for reduced etoh production	n-buoh and acetone 2:1	Semi batch "AB" Fermentation	Carbon dioxide stripping continuous in situ removal followed by distillation trains	2009 300 liter bench 2010 10,000 liter pilot
Butyl Fuel	Clostridium Aceto & tyro	GMO & mutant strain	n-buoh	Continuous two stage dual path anaerobic fermentation	stripping following immobilized cell bioreactors	Unknown
Syngas Biofuels Energy	Fermentation of Syngas	GMO	n-buoh	Thermochemical catalyst	NA	Unknown

Table 3-5. International Butanol Company Status

Company	Bug	Bug Strategy	Molecule	Fermentation Process	Separation Strategy	Development Status
Butamax (DuPont/BP)	1.Clostridium 2.E.Coli	GMOs	iso-buoh	Semi batch	continuous in situ removal followed by distillation trains	2010 Salt End Hull, UK 2013 Commercial Additional Feedstocks 2013+
Green Biologics (UK)		GMOs high tolerance (4%)	n-buoh	Continuous fermentation	In situ removal unknown.	Building demo in India. Consulting w/Chinese firms
Metex (FR)	"Well known bacteria"	GMOs	n-buoh	Unkown	In situ removal unknown.	Unknown
Butalco (Switzerland)	Yeast	GMOs	unclear	Unkown	In situ removal unknown.	Unknown
China	Clostridium	Currently selected strain. Migrating to GMOs	n-buoh	Migrating from traditional ABE Fermentation.	May include in situ removal	2010 100MM gpy traditional ABE. 201X migration beyond ABE. Plans to add 350 MM gpy new capacity.

Ramey and Yang (2004) provided some older estimates of the economic impact of producing Biobutanol versus ethanol. They estimated the investment required to build a complete facility for a 10 MM gal/yr butanol plant (base case) was \$1.56/gallon for a 20 year lifespan, with all support

facilities and 20 acres of land. They estimated the annual operating cost per gallon butanol to be \$0.15/lb, with the price of corn representing about 40% of this cost. They found that the economics for butanol production could be favorable relative to ethanol production, but their conclusion was primarily based on the fact that butanol is used as an industrial solvent that can be sold for 2.5 to 3 times more than ethanol.

Tao and Aden (2009) provide more recent estimates of the economics of producing biobutanol versus ethanol. In this work, these researchers developed a conceptual design for a number of different processes, including process relating to corn ethanol, sugarcane ethanol, soybean diesel, corn butanol, and biochemical and thermochemical processing of corn stover to ethanol. Aspen Plus was the process simulation software package used to generate the material and energy balance information for the processes. Comparisons were made for a plant scale of 45 MM gallon of production per year. The results showed a butanol production cost of \$1.96 per gallon, compared to the lower costs of \$1.53 and \$1.29 per gallon production costs for corn- or sugarcane-based ethanol production, respectively. Additionally, the total project investment of the butanol plant was nearly double that of the conventional ethanol plants due to the lower feedstock yield and more complicated separation process for the mixture of liquids produced. The costs of butanol become more favorable, however, when the energy difference between ethanol and butanol is accounted for. On an energy equivalent basis, the production cost of butanol was \$2.28 per energy equivalent gallon of gasoline, compared to production costs of \$2.33 and \$1.95 per energy equivalent gallon of gasoline, respectively, for corn- or sugarcane-based ethanol production.

3.2.3 *Infrastructure, Distribution, and Utilization*

3.2.3.1 Ethanol Infrastructure, Distribution, and Utilization

Ethanol is predominantly produced in the Midwest, as shown in Figure 3-3, by the color density under the production column. Consumption, on the other hand, is largely on the east and west coasts, as shown in Figure 3-3 by the blue color density under the consumption column for the low blend ethanol stations. In 2008, 14% of the ethanol for transportation use was used in California, Oregon, and Washington, and 36% was used by eastern seaboard states (EIA, 2010). Thus, ethanol must be transported to the east and west coasts where the predominant portion of the use is. Ethanol is currently not shipped by pipeline due to ethanol's special chemical properties. First, ethanol has material incompatibility issues with current existing petroleum pipelines, which will corrode and crack with long time ethanol exposure. Second, ethanol is extremely soluble in water, and thus it will absorb any water it comes in contact with in the pipeline distribution system. If gasoline/ethanol blends were transported via pipelines, the ethanol would phase separate due to the water in the pipeline distribution system. Further, due to ethanol's solvent properties, ethanol will dissolve the buildups in the gasoline pipelines, which could cause filter plugging (Curtis, 2008). Due to the limitations in pipelining ethanol, ethanol is transported long distances by rail and tanker trucks, and then blended at terminals before going to market. According to the U.S. Department of Agriculture, 60% of ethanol is transported by railroads, 30% of ethanol is delivered by tanker trucks, and the remaining 10% is transported by barges. The infrastructure for the transport of ethanol via railroads, tanker trucks, and barges, and the terminals for blending ethanol are shown in the transportation column in Figure 3-3.

Although large scale ethanol delivery through a pipeline is impractical, Kinder Morgan successfully shipped a test batch of 5,000 barrels of commercial denatured ethanol along with gasoline in its 16-inch Central Florida Pipeline (CFPL) from Tampa to Orlando in December 2008 (Kinder Morgan, 2009). This was the first time an ethanol-gasoline blend had been transported via an existing petroleum pipeline in the United States. Kinder Morgan is also currently evaluating the feasibility of transporting ethanol through its Plantation Pipeline in the southern part of the US. Several companies have been making an effort to investigate the feasibility of constructing dedicated pipelines to ship ethanol from the Midwest corn ethanol production plants to the east coast where larger quantities of gasoline are consumed. POET, the largest producer of ethanol in the country, and Magellan Midstream Partners, a pipeline-building company, have proposed an 1,800 mile, dedicated ethanol pipeline system would carry ethanol from production facilities in Iowa, South Dakota, Minnesota, Illinois, Indiana and Ohio to serve terminals in major Northeastern markets (Whitford, 2010). The cost of this pipeline is estimated to be \$3.5 to \$4 billion. The US DOE (2010) evaluated the viability of a dedicated ethanol pipeline from the Midwest to the East coast of the US. The DOE found that to be economically viable the pipeline would need to either carry 4.1 billion gallons of ethanol a year, as opposed to the currently projected 2.8 billion gallons a year, or, at the currently projected volumes, would need to charge an average tariff of 28 cents per gallon, which is substantially more than the current average rate for ethanol transport using rail, barge, or truck along the same corridor (19 cents per gallon).

While the refueling stations that sell low blend ethanol fuels are widely distributed through the United States, the number of stations that offer E85 is very limited. The distribution of dots in Figure 3-3 under the consumption column shows that most E85 refueling stations are concentrated in the Central United States. In contrast, most gasoline is consumed along the East and West Coasts. For example, there are only 43 E85 retail stations in California, where the consumption of gasoline is the highest in the nation. Further, only about 1,900 out of 170,000 refueling stations in the United States currently offer E85 (DOE, 2009c). The limited availability of E85 stations is an obstacle for the potential E85 users. E85 also cannot be stored and dispensed using the existing gasoline stations typical equipment without modifications, due to ethanol's chemical properties. The lack of ethanol station infrastructure development for the dispensing of E85 is one of the barriers to widespread use of E85.

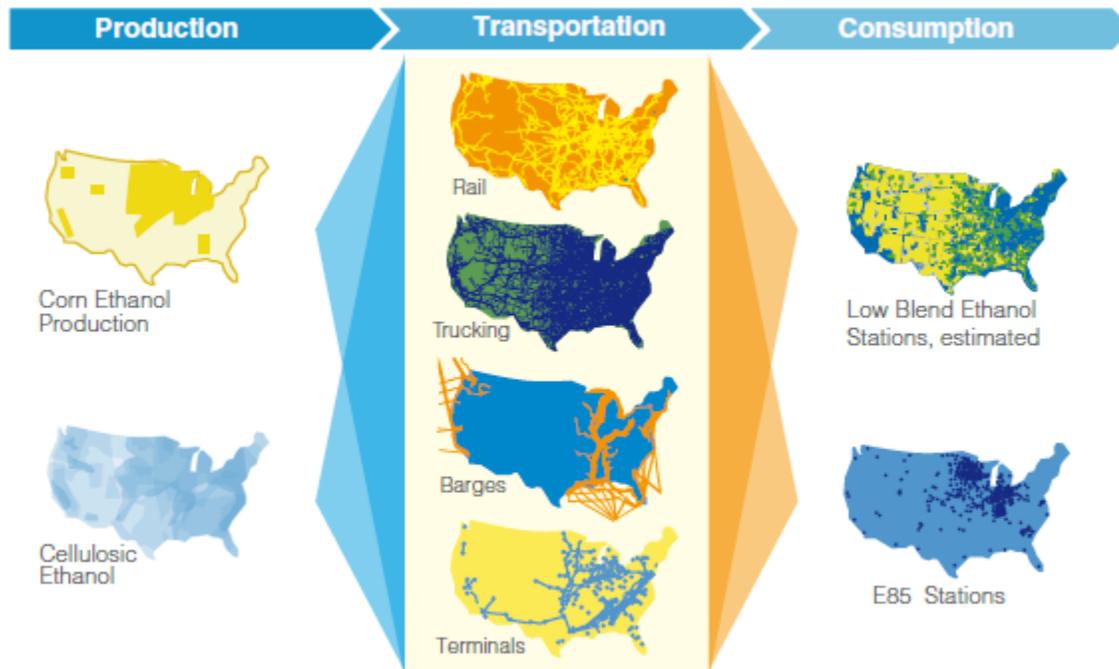


Figure 3-3: Industry Landscape of Ethanol

The consumption of ethanol today is predominately in the low-blend ($\leq 10\%$) form in conventional gasoline vehicles. The consumption of intermediate ethanol blends ($>10\%$ and $<75\%$) and E85 is still very limited. The US EPA (2010) recently issued a partial waiver to allow the use of E15 for model year 2007 and newer light-duty motor vehicles. The EPA denied the waiver for E15 for model year 2000 and older light-duty motor vehicles, as well as all heavy-duty gasoline engines and vehicles, highway and off-highway motorcycles, and nonroad engines, vehicles, and equipment. The decisions on the applicability of a waiver to model year 2001 through 2006 light-duty motor vehicles is still under consideration, pending the availability of additional test data. It should be noted that while the waiver provides provisions for using E15 in newer vehicles, E15 would still have to go through a full approval and extensive approval process before it would be accepted as a legal fuel for sale in California. Additionally, since the use of E15 is prohibited in older vehicles, E15 would have to be made available through dedicated pumps to minimize the potential of misfueling the older vehicles. Issues such as concern about misuse by consumers, liability, whether their pumps are UL-approved for E15, and the likely cost for installing new pumps will likely be major obstacles to bring E15 to the retail market, especially in California. There may also be issues as to whether legislation is needed to enforce auto warranties when an owner uses E15.

Flexible fuel vehicles (FFVs) are capable of operating on ethanol blends up to 85%. These vehicles are specially designed to allow for the use of greater levels of ethanol. Some of the issues addressed in the design of FFVs are: (1) the incompatibility of ethanol with some elastomers used in conventional gasoline vehicles (which can lead to elastomers swelling and degrading, and leaking hoses), (2) the potential for engine and fuel injector surface corrosion due to the high solubility of water in ethanol, and (3) the potential for some metal corrosion in the engine and fuel system due to the increase of the fuel electrical conductivity. FFVs qualify as

alternative fuel vehicles under the Energy Policy Act of 1992 (EPACT 1992) and are certified by the Environmental Protection Agency (EPA). FFVs are designed with modified components compatible with high concentrations of ethanol to ensure vehicle performance and durability. Today, the more than 8 million FFVs on U.S. roads constitute only ~2% of the total in-use passenger vehicles (DOE, 2009d).

FFVs are offered by several U.S. and some foreign-based vehicle manufacturers, including Ford, General Motors, and Chrysler. The retail prices for the FFVs are similar to conventional gasoline vehicles. Aftermarket conversion of a conventional gasoline vehicle to run on E85 is technically possible and the EPA has a process by which manufacturers of conversion systems can obtain a Certificate of Conformity for converted vehicles. The certification process may involve EPA testing of converted vehicles prior to issuing the certificate and certification applies only to the listed vehicles, not the conversion system by itself. Using non-certified conversions is illegal and may affect warranties. Vehicles operating in California must follow conversion rules issued by the California Air Resources Board (CARB, 2008). The cost of the conversion kit ranges from \$250 to \$380 depending on the vehicle model.

3.2.3.2 Butanol Infrastructure, Distribution, and Utilization

In comparison with ethanol, butanol has several advantages as a transportation fuel (BP and Dupont, 2010). Because butanol has a longer hydrocarbon structure than ethanol, it is fairly non-polar and more similar to gasoline than ethanol. Its energy content is higher than that of ethanol (105,000 Btu per gallon versus 84,000 Btu per gallon in ethanol) and hence is more similar to gasoline. Thus, biobutanol would have less of an impact on fuel economy and provide equivalent or better performance. Butanol, similar to ethanol, also has a higher octane rating than gasoline that could allow for greater compression ratios and higher efficiencies.

The compatibility of alcohol-based fuels with conventional fuel system components is also an important consideration. Currently, biobutanol can be blended up to 11.5% in the US with the potential to increase up to 16% by volume, with a 10% volume percent blending limit in Europe. Butanol has a lower vapor pressure than ethanol and therefore butanol/gasoline blends have a lower vapor pressure than corresponding ethanol/gasoline blends. The vapor pressure of ethanol at 20 and 30 °C is 9 and 14 kPa, respectively, whereas the vapor pressure of butanol at 20 and 30 °C is 5.4 and 8.7 kPa, respectively (Engineers Edge, 2010). There are some vapor pressure co-blend synergies with butanol and gasoline containing ethanol that could facilitate ethanol blending.

Butanol is potentially suitable for transport in pipelines, unlike ethanol (BP and Dupont, 2010). Thus, there is a potential to avoid the complication of terminal blending, as with ethanol. Butanol/gasoline blends are also less susceptible to separation due to water contamination than ethanol/gasoline blends. This makes butanol more compatible with the existing distribution infrastructure for petroleum fuels.

3.3 Technological Limitations and Commercialization of Conventional Alcohols

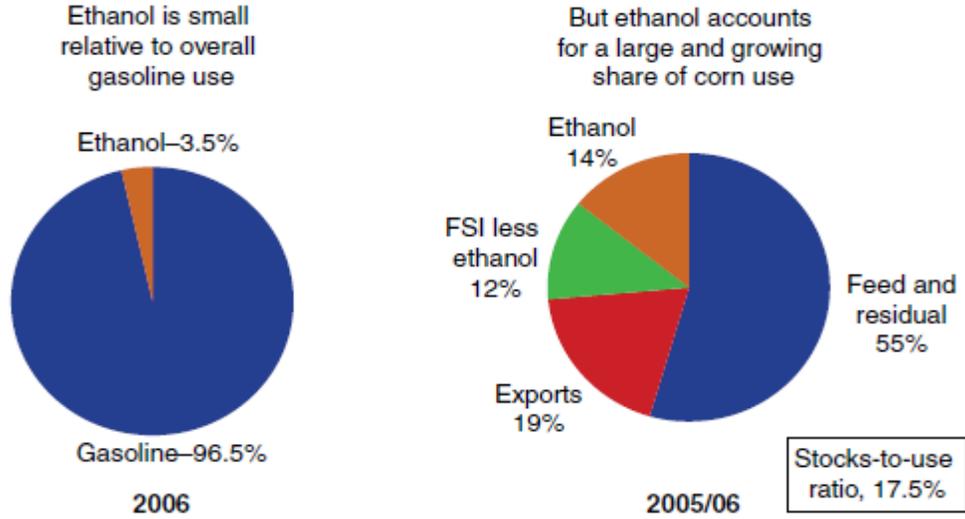
3.3.1 Limitations with Feedstock Availability and Other Production Constraints with Conventional Ethanol

One of the most important limitations with the expansion of starch- or sugar-based ethanol is the availability of corn and sugarcane feedstock. These limitations are further exasperated by the fact that these crops also play an important role in food production. The impact of ethanol fuel use on the agriculture sector is also fairly significant for only a limited offset of gasoline use. For 2009, for example, about one-third of the U.S. corn crop went to ethanol production, but this represented only 8% of the use of gasoline in the country on a volumetric basis, and an even lower fraction on a energy basis. Ethanol's role in the gasoline market and its effect on corn usage is illustrated in Figure 3-4. It is also important to note that due to ethanol's lower energy content that greater quantities of ethanol will be required to provide an equivalent energy content to the replaced gasoline gallons.

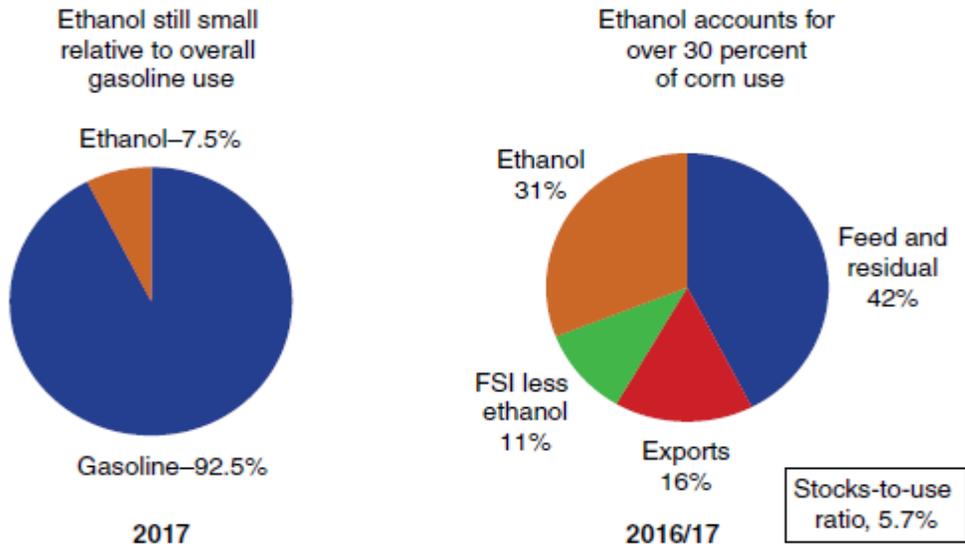
As more of the corn crop is used by the ethanol industry, corn prices will likely increase. Higher corn prices will also have an impact on corn's role as animal feed. In 2005/6, 55% of the corn crop was used as livestock feed, while the projection is that corn for animal feeding in 2017 will be reduced to 42% (Westcott 2007). Since corn plays an important role in feed for livestock, higher corn prices will result in reduced profits from meat production. Driven by the high profit of ethanol, production of other feed crops, such as soybean and sorghum, may decline, because all these crops compete for the agricultural land (Malcolm et al., 2009). Corn production for 2010/11 is projected at a record 13.4 billion bushels, up 260 million bushels from 2009/10. A total of 88.8 million acres of land will be used to cultivate corn. While the high price of corn brings farmers more income, retail food prices will rise faster than general inflation.

Wisner (2008) estimated the price of corn for the 2007-2008, 2008-2009, and 2009-2010 calendar years based upon the use of ethanol at actual levels versus the price if the use of corn for fuel production had remained at their level in 2004-2005 levels. His estimates are shown in Table 3-6. He concluded: "While it is impossible to identify the precise contribution of the ethanol expansion to the sharp increase in corn prices since 2004-05, it clearly has had a major impact."

Current relationships



Projected relationships in 10 years



Note: FSI = food, seed, and industrial.

Source: *USDA Agricultural Projections to 2016*, February 2007.

Figure 3-4: Ethanol's Role in Gasoline and Corn Market

Table 3-6: Estimated price of corn with and without increased use in fuels

		2007-2008	2008-2009	2009-2010
US weighted avg. farm price	Corn, actual ethanol level	\$4.25	\$5.40	\$5.40
US weighted avg. farm price	Corn, 2004-2005 ethanol level	\$1.75	\$1.60	\$1.40

There are uncertainties in estimating the impact of ethanol fuel use on food prices, however. In May of 2008, farmers and ethanol producers stated that corn for ethanol only increased food costs by 4 percent, while the Department of Agriculture said the figure is closer to 20 percent (Perrone, 2008). Renewable Fuels Association President Bob Dinneen cited analyst reports that rising oil prices have had twice the impact on food prices as rising corn prices (Perrone, 2008). Korves (2008), in a study for the ethanol industry, also suggested that with no increase in harvested corn acreage from the 2007 level of 85 million acres and growth in other uses of corn, the corn available for use in ethanol production could be 12 billion bushels by 2030, in comparison with only 2.2 billion bushels for the 2006 crop. This potential growth in the corn ethanol market is predicated on increases in corn yields, declines in the amount of nitrogen that will be needed per bushel of corn, and that ethanol plants will continue to improve efficiencies and reduce the amount of fossil fuels used per gallon of ethanol produced.

Sugarcane is another feedstock with a well established technology for production of ethanol. Currently, in the US, only Florida, Louisiana, Texas, and Hawaii grow sugarcane, and it is processed into sugar, which is more profitable than processing it into ethanol (Jacobs, 2009). In 2007, 27,750,600 tonnes of sugarcane was produced in the US (United Nations, 2009). If all of this sugarcane had been used to produce ethanol it would have yielded 1.94 billion liters (513 million gals). For comparison, gasoline usage for the US in 2008 was 137.8 billion gals (EIA, 2009). The annual gasoline consumption in California from 2002 to 2007 was 15,584,000,000 gallons (Californian Board of Equalization, 2009). If all the sugarcane had been used to produce ethanol there would only be enough to replace 0.37% of the US gasoline consumption, and if it had all been used to treat California gasoline it would only be enough to replace 3.3% of California's gasoline consumption.

The limitations of the sugarcane industry also have an impact on the economics of sugar-based ethanol production vs. starch-based ethanol production in the US. Table 3-7 shows estimated ethanol production costs from Shapouri and Salassi (2006) of the United States Department of Agriculture (USDA). These estimates show that while sugarcane-based ethanol from Brazil is cheaper to produce than corn-based ethanol from the US, the production of ethanol from sugar-based feedstock in the US is more expensive than corn-based ethanol production in the US. As shown in the Table, this finding is primarily related to the higher cost of the sugarcane or sugar beet feedstock. It should also be noted that although ethanol from Brazilian sugarcane is less expensive to produce than corn-based ethanol in the US, Brazilian ethanol is not imported to meet the US ethanol fuel needs because it is subject to a 54-cent per gallon tariff. This tariff, which runs through the end of 2010, is in place to offset the 45-cent per gallon blender's federal tax credit, that is applied to all ethanol regardless of its country of origin. Otherwise, the importing of Brazilian ethanol would receive the same subsidy that applies to domestically produced corn-based ethanol.

Table 3-7: Summary of estimated ethanol production costs (dollars per gallon)¹

Cost Item	U.S. Corn wet milling	U.S. Corn dry milling	U.S. Sugar cane	U.S. Sugar beets	U.S. Molasses ³	U.S. Raw sugar ³	U.S. Refined sugar ³	Brazil Sugar Cane ⁴	E.U. Sugar Beets ⁴
Feedstock costs ²	0.4	0.53	1.48	1.58	0.91	3.12	3.61	0.3	0.97
Processing costs	0.63	0.52	0.92	0.77	0.36	0.36	0.36	0.51	1.92
Total cost	1.03	1.05	2.4	2.35	1.27	3.48	3.97	0.81	2.89

1. Excludes capital costs.
2. Feedstock costs for U.S. corn wet and dry milling are net feedstock costs; feedstock costs for U.S. sugarcane and sugar beets are gross feedstock costs.
3. Excludes transportation costs.
4. Average of published estimates.

Another issue with developing corn or sugarcane crops for fuel use is the water use. Growing corn requires approximately 4000 gallons of water per bushel of corn during the growing season (RFA, 2009). In California, the water for growing corn would have to be provided primarily by irrigation.

Chiu et al. (2009) estimated the total water used for growing corn and processing it to produce ethanol for 19 states in 2007. The total water use ranged from a low value of 5 l water/l ethanol for Ohio to 2,138 l water/l ethanol for California. The authors note that according to a survey by the US General Accounting Office (GAO) in 2003, varied degrees of water shortages are expected within the next decade for 36 out of 47 states. All the high ethanol water usage states in the Chiu et al. study “were those classified in the GAO survey as to be likely to experience statewide (Colorado), regional (Wyoming), local (Kansas and Oklahoma), or uncertain water shortages (California and New Mexico). Continued expansion of corn production in these regions is likely to further aggravate expected water shortages of the region“. Chiu et al. also note that there is a mandate for conventional biofuel production to use no more than 57 billion liters of water by 2015 (EISA, 2007). In this regard, there is only limited additional water use capacity since the water use mandate is 90% filled by Biorefineries currently operating or under construction.

If corn replaces some other crop for the purpose of ethanol production, then to minimize the impact on water usage it should replace a high water usage crop. The California Department of Water Resources (2009) has data for irrigated crop acres and water use for 10 hydrologic regions in California for the years 1998 thru 2001. The applied irrigation water in acre-foot per acre for 2001 is provided in Appendix B. Grains, safflower, vines, and melons use the least water, and pasture, alfalfa, and rice use the most water. Water use for corn and other agricultural products are intermediate water users. Therefore, if corn for ethanol were to replace some other crop, then using land currently used for pasture, alfalfa, or rice would minimize the impact on water usage since these three crops require more water than corn.

The issue of water use for sugar-based ethanol production is even more important, since starch-based ethanol production takes ≥ 3 times as much water as corn to grow. This is shown in Table 3-8 (Rajagopal and Zilberman 2007). Thus, the water issues in California for sugar-based ethanol production would be even more significant than for corn-based ethanol production.

3.3.2 *Technical Limitations with the Production of Conventional Alcohols*

The production of ethanol is a relatively mature process, so this does not appear to be a significant limitation to the expansion of conventional ethanol for transportation fuels. The production of butanol via fermentation, on the other hand, is not widely used on a commercial scale, and is not cost competitive with conventional petroleum refining processes for butanol production. Further development and research, such as that described in section 3.2.23 and section 3.5, is needed to develop a process that is more economically competitive. The modification of current ethanol plants to produce butanol would also help to facilitate the production of greater volumes of butanol.

Table 3-8: Land and water intensity of potential sources for ethanol

<i>Ethanol feedstock</i>	<i>Global acreage (million hectares)*</i>	<i>Water required (mm/yr) (low)**</i>	<i>Water required (mm/yr) (high)**</i>	<i>Crop yield (tonnes per hectare)*</i>	<i>Ethanol conversion efficiency (litre/ton)***</i>	<i>Gasoline equivalent ethanol yield (litre/hect)</i>	<i>Ethanol yield per unit of water (lit/mm)</i>	<i>Growing season (months)</i>
Wheat	215	450	650	2.8	340	600	1.09	4-5
Maize (corn)	145	500	800	4.9	400	450	0.69	4-5
Sorghum	45	450	650	1.3	390	450	0.82	4-5
Sugarcane	20	1500	2500	70	70	3300	1.65	10-12
Sugar beet	5.4	550	750	100	110	7370	11.34	5-6
Sweet Sorghum	insig.	450	650	40	70	1900	3.45	4-5
Bagasse*	Na	Na	Na	18.9	280	3550	na	na

* estimates that are typically cited, **na** - data not available or not applicable, **insig.** - not significant
* data from FAO online statistical database
**data from FAO crop management database
<http://www.fao.org/ag/AGL/AGLW/watermanagement/default.stm>
*** data from various sources

3.3.3 *Technical Limitations with the Distribution and Utilization of Conventional Alcohols*

3.3.3.1 Ethanol Infrastructure, Distribution, and Utilization

One of the most significant technical limitations on the use of ethanol as a transportation fuel is the limitations on the level of ethanol that can be blended with gasoline. Current regulations limit the proportion of ethanol to 10-15% percent, depending on the model year, due to concerns regarding the compatibility of conventional internal combustion engines at higher blend ratios. Currently, there are 43 million 2007 and newer vehicles in the US that have now been approved by EPA to use E15, or approximately 20% of the fleet (Pore, 2010). A total of 86 million cars/light-duty trucks, or about 54 percent of all vehicles on the road today, are model year 2001 to 2006, that could be eligible to E15 pending further EPA consideration. The expanded use of E15 to this subset of vehicles, however, will face a number of obstacles, as discussed above. This includes the regulatory approval process that fuels must undergo in California to be legal for sale, and the development of segregated pumps so that E15 would not be misused in older vehicles, that represent a relatively small percentage of the vehicle fleet. Evaporative emissions are another issue for ethanol blends, as discussed further in sections 3.4 and 3.5.

The use of higher levels of ethanol, such as the 85% levels used in FFVs, will be limited by both vehicle availability and infrastructure. As discussed above, the FFVs must be specially designed to address the incompatibility of such high levels ethanol with conventional gasoline vehicles. Currently, FFVs account for only 2% of the in-use vehicle fleet in the US (DOE, 2009d), with slightly higher percentage populations in California. The availability of only 43 E85 retail stations in California is also a considerable limitation on how effective such vehicles would be in expanding ethanol use, even if FFVs were available in greater numbers in the fleet.

Ethanol also presents logistical challenges for distribution. The fact that large scale delivery of ethanol through pipelines is impractical represents an important limitation if ethanol were to be the predominant alternative fuel for future transportation. This would have a negative impact in the need for greater rail and truck transport. Similarly, while ethanol terminal blending is viable, and already being used on a relatively large scale, it is less than optimal. Dedicated ethanol pipelines are also a possibility, although this would likely be a costly proposition.

Another limitation with ethanol is its energy density. For identical volumes, ethanol contains approximately 30% less energy than gasoline depending on the gasoline formulation. One gallon of E85 contains 23% to 28% less energy than a gallon of gasoline (Johnson and Taconi, 2007), which reduces the fuel economy of E85-powered vehicles by about 25%. Additionally, a larger fuel tank capacity than that of gasoline fuel tank is required for operating E85 in order to run the same distance.

3.3.3.2 Butanol Infrastructure, Distribution, and Utilization

Butanol has several advantages relative to ethanol from a utilization perspective since it is a longer, fairly non-polar hydrocarbon. Butanol would have less of an impact on fuel economy compared to ethanol, given its 25% higher energy content on a per gallon basis, but butanol still provides a lower fuel economy relative to gasoline. More research is needed on other issues such as the compatibility of butanol with conventional vehicles and the existing infrastructure. There

is the possibility of transporting butanol by pipeline, but this issue has not been extensively studied (BP and Dupont, 2010). Butanol could potentially be more compatible at higher blend levels in conventional gasoline vehicles than ethanol, or offer co-blending synergies with ethanol. The current blend level of butanol is only slightly greater than those for ethanol, however, with a blend limit of 11.5% in the US with the potential to increase to up to 16% by volume. Additional research is needed to determine if butanol use in gasoline should be limited to values only slightly higher than those applicable for ethanol or if much higher levels of butanol would be compatible with gasoline vehicles. Similarly, little work has been done on co-blended butanol-ethanol mixtures and their potential compatibility with either conventional gasoline vehicles or FFVs.

3.4 Environmental and Other Considerations

One of the most important considerations in evaluating the environmental impact of the use of conventional alcohols for transportation use is its effect on GHG emissions. CARB (2009b) evaluated the Well to Wheel (WTW) GHG emissions for various scenarios of corn and sugarcane ethanol production using the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model, modified for use in California (CA-GREET) version 1.8b along with the Global Trade Analysis Project (GTAP) model for fuels produced from crops. These results are provided in Table 3-9. One of the most critical considerations in the development of the carbon intensity values was the impact of indirect land use changes, which occur when non-agricultural land is converted to agricultural uses in response to increased demand for biofuels. CARB used the GTAP model to estimate the effect of land use changes on GHG emissions for corn ethanol. They performed a sensitivity analysis involving 6 scenarios and estimated land-use corrected (LUC) carbon intensity values ranging from 18.3 to 44.3 with an average of 30 gCO_{2e}/MJ over 30 years. For the corn-based ethanol, when the land-use corrections were applied, the results showed that midwest corn had a slightly higher carbon intensity, depending on the process method, than the baseline gasoline. The only slightly favorable scenarios for Midwest corn-based ethanol production were for dry mill processes that either used biomass as a portion of the energy source, or utilized the distiller grain with soluble (DGS) byproduct in wet form, i.e., without drying. The average carbon intensity for California produced corn-based ethanol was very similar to, but slightly less than those for the average Midwest corn-base ethanol and for the baseline gasoline. The production of ethanol from Brazilian sugarcane is more promising, with all scenarios showing a carbon intensity benefit relative to either gasoline or corn-base ethanol, even with land use change considered.

Table 3-9: Adjusted Carbon Intensity Values for Gasoline and Ethanol from Corn and Ethanol from Sugarcane.

Fuel	Pathway Description	Carbon Intensity Values (gCO ₂ e/MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Gasoline	CARBOB – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	95.86	0	95.86
Ethanol from Corn	Midwest average; 80% Dry Mill; 20% Wet Mill; Dry DGS	69.40	30	99.40
	California average; 80% Midwest Average; 20% California; Dry Mill; Wet DGS; NG	65.66	30	95.66
	California; Dry Mill; Wet DGS; NG	50.70	30	80.70
	Midwest; Dry Mill; Dry DGS, NG	68.40	30	98.40
	Midwest; Wet Mill, 60% NG, 40% coal	75.10	30	105.10
	Midwest; Wet Mill, 100% NG ₁	64.52	30	94.52
	Midwest; Wet Mill, 100% coal ₁	90.99	30	120.99
	Midwest; Dry Mill; Wet, DGS	60.10	30	90.10
	California; Dry Mill; Dry DGS, NG	58.90	30	88.90
	Midwest; Dry Mill; Dry DGS; 80% NG; 20% Biomass	63.60	30	93.60
	Midwest; Dry Mill; Wet DGS; 80% NG; 20% Biomass	56.80	30	86.80
	California; Dry Mill; Dry DGS; 80% NG; 20% Biomass	54.20	30	84.20
	California; Dry Mill; Wet DGS; 80% NG; 20% Biomass	47.44	30	77.44
Ethanol from Sugarcane	Brazilian sugarcane using average production processes	27.40	46	73.40
	Brazilian sugarcane with average production process, mechanized harvesting and electricity co-product credit ₁	12.40	46	58.40
	Brazilian sugarcane with average production process and electricity co-product credit ₁	20.40	46	66.40

DGS = distillers grain with solubles

The inclusion of land-use change effects in the CARB carbon intensity estimates and the magnitude of these effects has been the source of some controversy. Some researchers, such as Fargione et al. and Searchinger et al., have argued that ethanol use for fuel could have a negative impact on GHG emissions if native habitats are converted to support expanded growing of corn. Fargione et al. (2008) estimated the “carbon debt” (the amount of CO₂ released during the first 50 years of this process) for several scenarios worldwide. For corn ethanol raised on converted US Central Grassland or Abandoned Cropland they estimated the carbon debt as 93 and 48 years, respectively. They conclude that the net effect of corn production via clearing of carbon rich habitats increases CO₂ emissions for decades or centuries relative to emissions caused by fossil fuel use. Searchinger et al. (2008) concluded that converting forests and grassland to new cropland for corn-based ethanol doubles GHG over 30 years. Table 3-10 below, from their article, summarizes the GHG contributions for life cycle processes. Note that their estimate of 104 gCO₂e/MJ is considerably higher than the estimates obtained by CARB.

Gallager (2008) reviewed the above reports and many others for the government of the United Kingdom. His report suggests that biofuels should continue to be pursued, but that more caution and discrimination are needed in advancing biofuels. Some of the estimates reviewed by

Gallagher that included land-use changes are in a similar range to the CARB values. Gallagher reports that Plevin et al. (2008) examined the uncertainty in the Searchinger et al. (2008) report and concluded that including indirect land-use change the estimated GHG emissions of corn ethanol at 95% confidence were 73 – 150 gCO₂e/MJ and the average value of 107 gCO₂e/MJ is still worse than emissions from gasoline (c 90 gCO₂e/MJ). Gallagher also reports that Fritsche (2008) has evaluated the GHG potential including use of an Indirect Land-Use Change (ILUC) factor. For a minimum, medium, and maximum ILUC factor, the estimated GHG emissions of corn ethanol are 72, 101, and 129 gCO₂e/MJ, respectively. Hertel et al. (2010) analyzed GHG emissions from corn ethanol production including land-use change and factoring in market-mediated responses and by-product use and these researchers came up with an estimate for land-use change value of 27 gCO₂e/MJ, similar to the CARB values.

Others, including the ethanol industry, have argued that the data available to estimate land-use change is inadequate and not sufficiently reliable or that the model methods are not sufficiently developed in some studies (Kruse et al., 2008; Wang and Haq, 2008; GAO, 2009). This could include consideration of drivers for land-use change aside from increased biofuels use, the large variation in the estimates of carbon released during land clearing, and difficulties in estimating how agriculture might be impacted by changing world policy (Kruse et al., 2008). It has also been suggested that the CARB estimates may not account for potential technology and productivity improvements (Zhang et al., 2010). Other considerations may have a more negative impact on land-use; however, such as the impact of potential global warming trends any associated drought or reduction in crop land.

Another controversial subject is the effect on GHG from fertilizer use. Crutzen et al. (2008) concluded that for biomass based sources that require fertilizer to promote growth, the N₂O emissions from the fertilizer may completely offset the GHG cooling effect of the reduced CO₂ emissions.

Table 3-10: Comparison of corn ethanol and gasoline greenhouse gasses with and without land-use change*

Source of fuel	<i>Net land-use effects</i>						
	Making feedstock	Refining fuel	Vehicle operation (burning fuel)	Feedstock carbon uptake from atmosphere (GREET)	Land-use change	Total GHGs	% Change in net GHGs versus gasoline
Gasoline	+4	+15	+72	0	–	+92	–
Corn ethanol (GREET)	+24	+40	+71	–62	–	+74	–20%
						+135	+47%
						without feedstock credit	without feedstock credit
Corn ethanol plus land use change	+24	+40	+71	–62	+104	+177	+93%
Biomass ethanol (GREET)	+10	+9	+71	–62	–	+27	–70%
Biomass ethanol plus land use change	+10	+9	+71	–62	+111	+138	+50%

* Comparison is by stage of production and use (grams of GHGs CO₂ equivalents per MJ of energy in fuel). Figures in total column may not sum perfectly because of rounding in each row. Land-use change was amortized over 30 years. Dash entries indicate “not included.” Calculated with GREET 1.7(4) using default assumptions for the 2015 scenario. Gasoline is a combination of conventional and reformulated gasoline. Ethanol rows are based on E-85 and adjusted to isolate effects of ethanol by proportionately removing emissions of gasoline. Land-use change emissions are amortized over 30 years and for biomass assume use of US corn fields of average yield to produce switchgrass at 18 metric tons/ha with no feed by-product. Emissions from burning ethanol are slightly higher than feedstock uptake credit because some carbon is emitted as more potent GHGs than CO₂. By GREET estimates, 3.04 MJ provides power for 1 km.

Another element of lifecycle GHG emissions are the CO₂ emissions during ethanol production, which are accounted for in the lifecycle analyses. CO₂ emissions from a dry mill ethanol plant arise from the fermentation process and the on-site combustion of fossil fuels for generating steam and heat for the process vessels. The US EPA estimates that fossil-based CO₂ emissions associated with ethanol production at dry mill ethanol facilities are approximately 5.3 pounds per gallon of ethanol produced (US EPA CHP Partnership, 2007). This figure does not consider the

energy consumed in growing, harvesting and transporting the feedstock, or in transporting the ethanol. It assumes no recovery of CO₂ and drying the wet distillers grain to 11% moisture content to be used for cattle feed. The amount of CO₂ produced per gallon of ethanol can be higher or lower than conventional gasoline production depending on the fossil fuels used for electricity, steam, and heating, as well as the energy efficiency of the plant. The CO₂ from the fermentation is very pure and can be used in food and beverage applications. Some dry mill facilities have been able to sell this co-product, but this largely depends on location and area demand.

Whether there is a net energy loss or gain from converting corn to ethanol, and whether or not ethanol increases or decreases GHG relative to gasoline has been another controversial subject. This includes two studies done in the 2004-2005 time period that reported negative net energy values (Patzek, 2004; Pimentel and Patzek, 2005). This is a particularly important issue, since if it requires more energy from non renewable sources to produce the ethanol than the energy that the resulting fuel provides, then the resulting fuel does not provide any benefits in terms of fossil fuel reduction. Farrell et al. (2006) reviewed six studies related to the energy inputs and outputs of ethanol from corn and greenhouse gas emissions (GHG), including the studies by Patzek and Pimentel and Patzek. They reevaluated each study correcting any input assumptions found to be in error and added a credit for coproducts in those studies where it was not included. The result of their evaluation indicated a range of net energy gain from -3.1 to 7.9 with a best estimate of 4.6. Farrell et al. attributed the negative net energy results found by Patzek and Pimentel and Patzek to incorrect assumptions that ethanol coproducts (materials inevitably generated when ethanol is made, such as dried distiller grains with solubles, corn gluten feed, and corn oil) should not be credited with any of the input energy and the use of some input data that was old and unrepresentative of current processes. They concluded that GHG emissions could be slightly higher or slightly lower for ethanol versus gasoline. They also concluded that “it is already clear that large-scale use of ethanol for fuel will almost certainly require cellulosic technology.”

The emission profile for ethanol is also important. Federal regulations require oxygenate addition to gasoline to reduce carbon monoxide (CO) and hydrocarbon (HC) emissions. Ethanol is the oxygenate of choice for meeting this regulations, as numerous studies have shown that ethanol reduces these emissions components, particularly in older vehicles. While ethanol reduces CO and HC emissions, it can increase evaporative emissions because the blend of gasoline and ethanol has a higher vapor pressure than either of the blend components.

Evaporative emissions are one important environmental consideration for ethanol blends. Evaporative emissions are the result of ethanol and gasoline vapors escaping from the vehicle's fuel system instead of tailpipe emissions. The sources of evaporative emissions are fuel permeation, liquid and vapor leaks, and fuel tank venting (canister losses) (Haskew, 2006), where tank venting and fuel permeation are in general the most important sources of evaporative emissions in a vehicle. Evaporative emission control systems are installed in all current vehicles to meet the EPA emission standards. It is known that the addition of ethanol to a HC base fuel causes an increase in the fuel Reid Vapor Pressure (RVP) (Caffrey and Machiele, 1994). Other factors which can contribute to higher evaporative emissions from ethanol blends include the higher permeability of ethanol thru the walls of fuel system components and the difficulty of purging ethanol from the carbon canisters (Martini, 2007). A number of earlier studies have

shown that low level blends of ethanol increase evaporative emissions (CARB, 1999; CARB, 1998; Reuter et al., 1992; Haskew & Associates, 2001). Some of the more recent studies related to evaporative emissions are discussed in the ongoing research section below.

3.5 Ongoing Research

3.5.1 Mid-Level Ethanol Blends Study

The US EPA and a number of other governmental and other agencies are still in the process of studying the potential impacts of using higher ethanol blends in gasoline vehicles on the durability of vehicle systems and emissions. The State of Minnesota and the Renewable Fuels Association (RFA) studied the effects and performance of E20 on modern vehicle engines and engine components, including drivability, material compatibility, fuel pumps, and sending units (Mankato, 2009; Mead et al, 2009; Jones et al, 2008a,b,c; Kittelson et al, 2008). These studies were done in response to a bill, signed by Minnesota Governor Tim Pawlenty, requiring that the state's total consumption of fuel include at least 20 percent ethanol or the use of 20 percent volume ethanol blended gasoline by 2013. The effects of E20 on automotive fuel pumps and sending units were also investigated (Kittelson, et al., 2008). For the drivability study, 40 pairs of vehicles consisting of 14 passenger cars and 66 light-duty trucks or vans were selected as pairs of the same year, make, and model that would have similar usage patterns. The fleet model years are from 2000 to 2006 with engine displacement ranging from 1.5 to 8.1 liters. The one calendar year road test results showed that E20 provided similar power and performance compared to E10. No significant difference in fuel economy was observed between paired vehicles powered with E10 and E20. The materials compatibility studies were conducted to compare the effects of E20 to E10 and E0 on plastics, metals and elastomers in vehicle and small engine fuel systems and fuel sending units. The studies tested eight different plastics, nineteen different metals, and eight elastomers used in automotive, marine, and small engine fuel systems and fuel dispensing equipment. No significant difference of materials compatibility was observed when E20 was compared to E10. The test results concluded that E20 fuels do not present problems for current automotive or fuel dispensing equipment. The tests to investigate the effects of E20 versus E10 and E0 on vehicle's emissions are not completed yet.

Another study to evaluate the impacts of intermediate ethanol blends on legacy vehicles and small non-road engines was conducted by NREL, to assess the viability of using intermediate ethanol blends to meet national goals of using more renewable fuels (Knoll et al., 2009). In the first stage of this project, tests were performed on 16 popular late-model vehicles and twenty-eight small non-road engines to evaluate the effects of E15 and E20 versus E10 and E0 on tailpipe emissions, vehicle drivability, and catalyst durability. During the time of the test period no operability and drivability issues were identified when vehicles were running E15 or E20. Test results showed fuel economy decreased commensurately with increasing ethanol content. Vehicles exhibited 7.7% fuel economy loss with E20 compared to E0. Emission results showed that regulated emissions were generally not affected by increasing ethanol content in the fuel. However, acetaldehyde and formaldehyde emissions increased with increased ethanol content. The catalyst temperature tests showed that catalyst temperatures were cooler or unchanged with higher ethanol content at closed-loop conditions. At wide-open throttle (WOT), seven of the

sixteen tested vehicles ran leaner and the catalyst temperatures were 29°C to 35°C higher with E20 compared to E0.

3.5.2 *Effects of Mid-Level Ethanol blends on ECM*

The Transportation Research Center Inc. (2009), under contract with the Coordinating Research Council, conducted a mid-level ethanol blends catalyst durability screening study to develop data on the durability effects of mid-level ethanol blends on emission control systems (CRC Report E-87, 2009). The first phase of this program was to identify vehicles with algorithms, termed used learned fuel trims, that correct open loop air-fuel ratios when operated on ethanol blends. In this program, twenty-five vehicles were selected, including twelve popular vehicles manufactured since 2000, and thirteen vehicles representing technologies that were manufactured since 1990, but were not thought to use adaptive fuel trim. The modified version of the European Program for Emission, Fuels, and Engine Technologies (EPEFE) Sulfur Purge Cycle was performed on the vehicles with four different fuels, E0, E10, E15, and E20. Test results showed that thirteen of the twenty-five vehicles did not adjust open-loop fueling to compensate for ethanol in the fuel, eight vehicles used leaned fuel to trim the open-loop fueling, and four vehicles were unclear. Of the 3.2 million registrations represented by the tested vehicles in this study, 53% did not appear to adapt to ethanol use, 31% appeared to adapt to ethanol use, and results were unclear for 16%. The thirteen vehicles that did not adjust open-loop fueling to compensate for ethanol may have the potential to degrade catalyst performance after extended operation on mid-level ethanol blends.

In an earlier study by the Orbital Engine Company in Australia (2004), however, it was found that 60% of the test vehicles did not use a fuel trim that adjusted for ethanol during open loop operation. In that study, all of these vehicles showed some level of catalyst performance deterioration after 50,000 miles of operation on E20.

3.5.3 *Ethanol Evaporative Emissions*

Harold Haskew & Associates, Inc and Automotive Testing laboratories have been studying evaporative emissions from later model vehicles (Haskew et al., 2004, 2006). The test results showed that ethanol blends of E20 and below increased fuel permeation emissions significantly in all test vehicle systems compared to E0 gasoline fuel. Vehicles with zero evaporative emissions systems (PZEV) or advanced technology LEV II and PZEV systems had much lower fuel permeation emissions than the vehicles (MY 2000-2001) with earlier enhanced evaporative systems for all testing fuels.

Several research studies have investigated the effects of ethanol content on evaporative emissions (Haskew, 2004, 2006; Martini, 2007). Coordinating Research Council, Inc. (CRC) contracted Harold Haskew & Associates, Inc and Automotive Testing laboratories to measure the permeation of MY2000 to 2005 California vehicles with gasoline containing various percentages of ethanol: E0, E6, E10, E20 and E85. In this project, five vehicle fuel systems were tested, including two California Enhanced Evap vehicles, a California LEV-II “near-zero” passenger car, a California PZEV Zero Evaporative Emission car, and a FFV capable of operating with unleaded gasoline, E85, or any blend level in between. The test results showed that ethanol blends level E20 and below increased fuel permeation emissions significantly in all test vehicle systems compared to E0 gasoline fuel. The vehicle with zero evaporative emissions

system (PZEV) had the smallest evaporative emissions increase due to ethanol among all the vehicles tested. Vehicles (2004 MY) with the advanced technology LEV II and PZEV system had much lower fuel permeation emissions than the vehicles (MY 2000-2001) with enhanced evaporative systems for all testing fuels. The project also concluded that the high-level ethanol blend (E85) tested in the flexible fuel vehicle system had lower permeation emissions than the non-ethanol (E0) fuel.

More recently, the CONservation of Clean Air and Water in Europe (CONCAWE), the European Council for Automotive R&D (EUCAR) and the Joint Research Centre of the European Commission jointly conducted tests to investigate the effects of gasoline fuel vapor pressure and ethanol content on evaporative emissions from modern passenger cars equipped with canisters, using the current European regulatory test procedure (Martini et al, 2007). The test results indicated that fuel vapor pressure is a key fuel variable for evaporative emissions. Several tests on one vehicle also showed that ethanol containing fuels with matched vapor pressure also gave higher evaporative emissions than the hydrocarbon fuels. More recently, CONCAWE, EUCAR and the Joint Research Centre of the European Commission jointly conducted tests to investigate the effects of gasoline fuel vapor pressure and ethanol content on evaporative emissions from modern passenger cars equipped with canisters as determined using the current European regulatory test procedure (Martini, et al, 2007). The test results concluded that fuel vapor pressure is a key fuel variable for evaporative emissions. Fuel vapor pressure above that of the 60 kPa DVPE (Dry Vapor Pressure Equivalent) increased evaporative emissions. Several tests on one vehicle showed that that ethanol containing fuels with matched volatility gave higher emissions than the hydrocarbon fuels.

3.5.4 *Conventional Ethanol Production*

There is also some ongoing research in the production of ethanol from corn via conventional processes. The Minnesota Corn Research & Promotion Council (MCR&PC) and the Initiative for Renewable Energy and the Environment (IREE) (Hamerlinck 2010) are funding five research projects in 2010. The projects are: (1) production of bio-char and bio-oil from the ethanol co-product distillers' grains; (2) investigate and evaluate equipment to densify bulk corn stover; (3) gasification of corn stalks, leaves, cobs, distillers' grains; (4) research on a new strain of high-oil corn to better understand the genetics; (5) assessment of raw carbon dioxide from ethanol plants fermentation process as a feedstock for algae.

Stakeholders at a symposium on "Biofuels, Water Resources and Climate Change: Solving the Sustainability Puzzle" held at the University of Nebraska (Cassman, et al, 2009) recommended the following research needs:

- Recent, relevant data and complete life-cycle analysis for quantitatively modeling the sustainability of biofuels.
- Determine optimal uses of land for production of all types of biofuel feedstocks in the High Plains region, where soils and climates differ widely. It should be noted here that PIER is already conducting research into the viability of different agricultural feedstocks in conjunction with the California Department of Food and Agriculture (CDFA).

- Increase the efficiency of the corn ethanol production process.
- Develop cellulosic ethanol and other second-generation biofuels.
- Improve yields for biofuel feedstocks – corn, soybeans and proposed second generation feedstocks such as switchgrass.
- Improve efficiency in consumptive use of water by ethanol plants.

3.5.5 *Conventional Butanol Production*

Over the past two decades, considerable research efforts have been devoted to the development of new butanol production technologies to improve the process economics. Techniques that have been investigated to improve the traditional ABE fermentation process include cell recycling and cell immobilization to increase cell density and reactor productivity, using extractive fermentation to minimize product inhibition, and genetic and metabolic engineering of *C. acetobutylicum* (Ramey and Yang, 2004). The potential of fermenting corn starch using genetically modified yeasts to produce butanol has also been studied. The Fermentation Biotechnology Research Unit of the USDA and other groups have researched butanol production from agriculture residues, including wheat straw, corn stover, barley straw and switch grass by simultaneous saccharification and fermentation using *Clostridium beijerinckii* (Quieshi, 2008). Other novel metabolic engineering approaches include the synthesis of branched-chain higher alcohols via non-fermentative pathways, such as amino acid biosynthesis (Atsumi et al., 2008).

3.6 **Research Roadmap Recommendations for Conventional Alcohol**

Conventional starch-based ethanol is a commercially mature process in the US. Due to the commercial status and widespread installation of conventional starch-based ethanol production technologies, there are few production technology limitations to further expansion of the industry. The starch-based process is relatively energy intensive and it is possible that development of biomass-powered combined heat and power at existing ethanol facilities could displace at least a portion of the fossil fuel requirements at typical production facilities. It is not expected that there would be any significant advances in this area that would dramatically improve the commercialization prospects of starch-based conventional ethanol production, however. The production of ethanol from sugar-based feedstocks is also essentially fully developed. These facilities have already demonstrated the ability to utilize process residues (i.e., bagasse) as a boiler fuel to avoid fossil fuel consumption. Because of these successes, there are few technical aspects of sugar-based ethanol processes that warrant additional research and development.

The main limitation for this technology appears to be the availability of feedstocks. Given that about one-third of the current US corn crop is going to ethanol production and that this only represents 8% of the gasoline use in the country, it does not appear that conventional ethanol production will expand significantly from current levels. Concern regarding the use of land and crops that could be used for human or animal food consumption will also likely hamper the growth of the conventional ethanol industry worldwide. It is possible that further research could be conducted in the development of starches from non-edible sources that might allow for the expansion of conventional ethanol in certain parts of the world, but it is uncertain that such

research would significantly impact the industry in the US. Similarly, it is possible variations of sugarcane and other sugar-rich feedstocks that are better-suited for colder and drier climates could be developed, but this should be a lower priority for PIER-funded research.

Some research funds could also be targeted toward evaluating the most cost effective methods for butanol production. Butanol has a number of advantages over ethanol, including its better compatibility with the petroleum infrastructure and vehicles and its higher volumetric energy content. Investing in determining the most cost effective method to produce biobutanol, whether by modifying existing ethanol facilities or building facilities from the ground up is justified.

The most important area of research for expanded use of ethanol in vehicles is addressing the current 10-15% regulatory limits on the level of ethanol that can be used in conventional gasoline vehicles. Such research would be of importance for both the expansion of conventional ethanol processes as well as the cellulosic ethanol processes that are targeted for most of the future growth in ethanol production. While EPA has approved the use of E15 in some newer vehicles, the continued restriction of the use of E15 in older vehicles will impose important limitations on the expansion of E15 use at a retail level, due to the need for separate pumps and other issues. If the market penetration remains at the 10% level, the EISA goals could not even be achieved. In the near term, research in the area of vehicle compatibility for higher levels of alcohol could focus on the potential to increase the blend limit from 10 to 15 or 20 percent for ethanol, but over a broader range of vehicles. Beyond that, it is possible to expand the broader use of other alcohol-based fuels, such as butanol, or mixtures of different alcohol blends. Fuels such as butanol would provide certain advantages over ethanol in terms of energy density and overall similarity with gasoline. Combinations of different alcohols, such as ethanol and butanol, might provide even more beneficial synergies. While such research might be beneficial, it is beyond the scope of topics that would be funded by the Alternative fuel section of the PIER-TRA. Such research would be more appropriately funded under the Vehicle Technologies section of the PIER-TRA, or by another outside agency or organization. In this regard, the PIER-TRA vehicle technologies section has recently initiated a program in this area that will be conducted by UCR (Durbin et al., 2010).

In summary, with the feedstock and other limitations, it is unlikely that the production of starch- or sugar-based alcohols for fuel will expand significantly beyond current levels. Hence, it is not recommended that funds be allocated towards research for this technology unless this research could also facilitate the commercialization of another more promising technology. The development of biomass-powered combined heat and power technologies would probably be the research that would be most applicable to other technologies.

4 Conventional Biodiesel

4.1 Introduction

The second most prevalent biofuels are those made from plant oils (Soy, Rapeseed/Canola (which is a genetic modification of rapeseed), Palm, Sunflower, and Castor) and animal fats. In the US, the primary source of biodiesel is soybeans. Biodiesel has grown in popularity over the past decade from 2 million gallons per year in 2000 to 711 million gallons per year in 2008 in the U. S. and from 213 million gallons per year in 2000 to 3,888 million gals per year in the world (Brown, 2009). The biodiesel production route refers to the commercially mature process of converting oils, fats, and greases into diesel via the transesterification process. The production of biodiesel from this conventional Fatty Acid Methyl Ester (FAME) process is a very well developed technology, with a large number of commercial facilities in operation. As shown in Table 4-1 (RISE, 2010), in 2005, Germany, France, United States, and Italy had the largest production capacities. In this chapter, the technical development and ongoing research for biodiesel as a transportation fuel are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for biodiesel are provided.

Table 4-1: World biodiesel Production by Country, 2005

World Biodiesel Production by Country, 2005	
Country	Production
	Million Litres
Germany	1,921
France	557
United States	284
Italy	227
Czech Republic	136
Austria	85
Spain	84
Denmark	80
Poland	80
United Kingdom	74
Brazil	70
Australia	57
Sweden	7
Other Countries	102
World	3,762
Source: F.O. Licht, "World - Biodiesel Production (tonnes)," table, World Ethanol and Biofuels Report , vol. 4, no. 16 (26 April 2006), p. 365, and the Earth Policy Institute.	

4.2 Development of Biodiesel as a Transportation Fuel

4.2.1 *Biodiesel Feedstocks*

Currently, the most common form of biodiesel is Fatty Acid Methyl Ester (FAME). The technology for FAME production is well developed. Nearly any oil or fat can be converted to FAME by transesterification with methanol in the presence of a catalyst. In the US, the major FAME feedstock is vegetable oils, and amongst the vegetable oils soybeans are the prime source. As in the case with ethanol, this primary source is also an important food source and therefore there is considerable research to find other more plentiful sources for making biodiesel. Animal fats are another source of FAME.

While the quality of finished biodiesel will vary somewhat depending on the level of hydrogen saturation, most of the finished products for a properly controlled production process will still be well within the range of acceptability for on-road transportation use. Since the biodiesel production process is relatively simple with a high yield of finished product, the majority of the production cost lies in the cost of the oil feedstock. Securing low cost, high quality oils is the most important factor behind the economic success of biodiesel facilities. The difference in price between crude vegetable oils and diesel fuel is a good indicator of the profitability of the biodiesel industry. Similar to conventional alcohols, the potential competition with the use of oils for food production is another limitation, as discussed in section 4.3.

4.2.2 *Biodiesel Production*

The vast majority of all biobased diesel produced in the world is through the transesterification of fatty acids to methyl esters (FAME). This process is shown in Figure 4-1. In this Figure, the glycerides represent the oils, fats, and greases. Reactions of these glycerides with methanol in the presence of a base catalysis, such as sodium or potassium hydroxide, converts the glycerides to methyl esters (biodiesel) and glycerol. The R's in Figure 4-1 are various complex hydrocarbon structures which differ depending upon the specific source of the oil, fat, or grease used in the process.

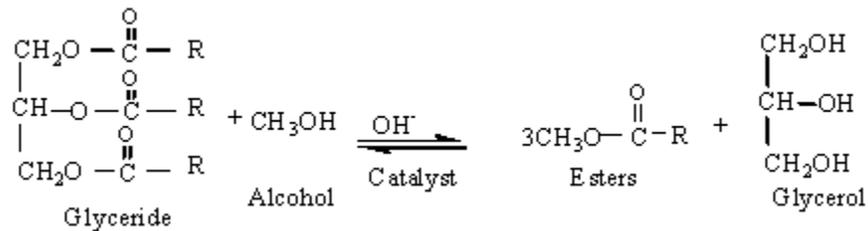


Figure 4-1: Transesterification Process

The transesterification process is simple, with a relatively low capital cost compared to most other biofuel production routes. The design and operation of FAME biodiesel plants is mature and well understood. Variation does exist for the process rate (batch versus continuous), drying and separation methods, and how the catalyst is introduced to the process. However, these differences are largely driven by the size and tradeoff between capital and operating cost. Larger plants do enjoy some economy of scale, but the differences are not as pronounced as for other technologies, such as some thermochemical processes.

The US Energy Independence and Security Act (EISA, 2007) mandated the production of specific volumes of renewable fuels for the years 2006 through 2022. For the years 2009, 2010, 2011, and 2012, the mandated volumes are: 11.1, 12.95, 13.95, and 15.2 billion gallons, respectively. Biomass-based diesel, which is predominantly biodiesel, is mandated to comprise 0.5, 0.65, 0.80, and 1.0 billion gallons for 2009, 2010, 2011, and 2012, respectively. Following 2012, the EPA administrator in coordination with the Secretary of Energy and the Secretary of Agriculture are to determine the required volumes of biomass based diesel. The 2009 mandate was achieved in 2007 for biodiesel and the 2010 mandate was exceeded in 2008. The EPA has also declared biodiesel an 'advanced biofuel' that provides over a 50% reduction of carbon emissions compared to petroleum based diesel fuel. This makes biodiesel eligible to meet another 4 billion gallons of advanced non-cellulosic biofuels requirements per year by 2022.

Hundreds of companies worldwide are involved in the production of biodiesel. Emerging Markets Online estimates that roughly 3 billion gallons of biodiesel were used worldwide in 2008. Worldwide production capacity, however, was 3 times this figure. On June 22, 2009 the National Biodiesel Board reported that there were 173 companies marketing biodiesel and they have an annual production capacity of 2.69 billion gals/yr (NBB, 2009a). They also noted that one plant is expanding their existing operations, which if realized, will result in another 427.8 million gals/yr. The actual estimated US Biodiesel production by fiscal year (Oct 1 – Sept 30) for 2008 was 700 million gallons (NBB, 2009b). During that fiscal year 65.20 billion gals of distillate fuel was produced, (see Table 3.2 in (EIA, 2009)). Assuming the ratio of diesel fuel to distillate fuel is approximately the same as in 2002 (In 2002 the total US distillate fuel was 57 billion gals and 40 billion gals was used as diesel fuel (Coltrain, 2002)) then 45.75 billion gals of this is diesel fuel. The 700 million gals of biodiesel could have treated the entire U. S. diesel fuel production to a level of 1.5% biodiesel.

The worldwide use of biodiesel grew through 2008, but oversupply, policy changes, and the economic slowdown of 2009 led to a decline in use. Although the US biodiesel use was estimated at 700 million gallons in 2008, it is projected to decline to less than half this number in 2009. The sharp drop-off in the production of biodiesel was due to a number of factors including (1) feedstock costs, (2) a credit crisis, (3) an economic recession, (4) a tariff imposition on US biodiesel into Europe, (5) a one year delay by EPA in the implementation of the RFS-2 rule, and (6) a campaign against biofuels on issue of sustainability (Jobe, 2009). This has led to an estimated 70 to 90 percent of US biodiesel capacity sitting idle as of early 2010. In addition, the loss of the blender's tax credit at the end of 2009 and uncertainty about its renewal has led to further production declines.

Biodiesel is also being developed as an alternative fuel for the heating oil market, as the heating oil industry looks to reduce petroleum use. Oilheat industry leadership, including the National Oil Heat Research Alliance, the New England Fuel Institute, and Petroleum Marketers Association of America, called for “all heating oil to be at least 2% by July 2010” at the National Oilheat Industry policy summit (NBB, 2009d). No. 2 diesel is used in about 8.1 million out of 107 million households in the US, with about 8 billion gallons of No. 2 diesel used per year for heating. Replacing traditional No.2 diesel with B5 for heating would increase biodiesel demand by 450 million gallons annually, resulting in significant reduction of petroleum heating oil (NBB, 2009d). Several state governors are working on new legislation to mandate biodiesel blends in heating oil. New York State passed a B2 heating oil mandate to begin in October of 2012. The state of Oregon provides a tax credit of up to \$200 for people who purchase home heating oil that is at least 20% biodiesel.

4.2.3 *Biodiesel Infrastructure, Distribution, and Utilization*

In general, biodiesel can be used in existing diesel engines and the refueling infrastructures with no modification. The allowable blend levels under warranty vary between different engine manufacturers, but all manufacturers at least warranty use of B5. Biodiesel blends can be delivered and stored with the current diesel fuel delivery methods and refueling infrastructures with little or no modification. Biodiesel is not delivered in pipelines in the US, however, due to its potential impact on jet. This limitation is particularly applicable to California, since nearly all of the California pipelines currently carry jet fuel. Therefore, biodiesel is typically splash blended. The use of biodiesel in pipelines in Europe is discussed in further detail below in section 4.3.

While biodiesel is generally compatible with the diesel engines, it does have some physical and chemical properties that require some special housekeeping during its use and handling such as, its solvency, low temperature engine operability, stability, and materials incompatibility. The quality of biodiesel blend fuels in the market, and vehicle warranty issues are other important issues. Emission measurements have shown that, the most common biodiesel, i.e., FAME has higher NO_x emissions than regular diesel. The higher NO_x must be mitigated for the fuel to become a viable fuel alternative for California.

The building blocks of biodiesel, methyl esters, are commonly used in solvent products and cleaners. When using biodiesel, there is some tendency for it to dissolve accumulated sediments in diesel storage tanks and engine fuel tanks. These dissolved sediments can plug the filters at the fuel dispensers or travel through the system and clog fuel filters at the engine. In some cases, injector deposits can lead to injector failure, but this is a rare occurrence. Most users of B20 typically do not clean their fuel tanks prior to use since B20 is sufficiently diluted to mute the solvent effect. It has been suggested that extra fuel filters be maintained on hand during initial use, since cases of filter plugging have been reported and are more likely in the first few tanks. The effects of B100 would be greater, so it is suggested that fuel tanks be cleaned and extra precautions be taken with the fuel system for B100 use (Biodiesel Handling and Use Guide, 2009).

Biodiesel can cause degradation, softening, or seeping through some hoses, gaskets, seals, elastomers, glues, and plastics with prolonged exposure. Concern about elastomer degradation is more critical for applications where B100 is used, as opposed to B20. Nitrile rubber compounds, polypropylene, polyvinyl, and Tygon are particularly vulnerable to B100. Materials such as Teflon, Viton, fluorinated plastics, and Nylon, on the other hand, are compatible with biodiesel. Older vehicles, manufactured before approximately 1993, are more likely to contain materials that could be affected by B100 over longer periods of time (Biodiesel Handling and Use Guide, 2009). Engines newer than 1993 and modern repair kits should contain biodiesel compatible materials, but not always. For use at more standard B20 blend levels, fleet experience has shown that material compatibility issues are minimal, even for elastomers made of materials such as nitrile rubber that are not compatible with higher biodiesel blends. Warranty repair is a key decision element when purchasing a vehicle or engine, and a customer expects the fuel used in their truck will not affect the repair under warranty provision. While the EMA states that manufacturers accept B5 for all engines, it also pointed out that individual engine manufacturers determine what implications, if any, the use of any fuel, including biodiesel, has on the manufacturers' commercial warranties.

Biodiesel has less favorable cold weather flow characteristics compared with conventional diesel fuel. Biodiesel fuels produced from feedstocks with highly saturated fatty acid structures (such as palm oil and tallow) have poorer cold weather operability than fuels generated from feedstocks with highly unsaturated fatty acid structures (such as; rapeseed and safflower oil) (Hoekman, 2009). Cold flow additives are available to mitigate these issues by inhibiting crystal formation, but they have varying degrees of success depending on the feedstock. NREL suggests that users specify to the blend supplier that the fuel remains crystal free at temperatures down to -14°F during the winter season (Biodiesel Handling and Use Guide, 2009). B20 has been used in cold temperature climates such as northern Minnesota and Wyoming, where temperatures regularly fall to below -30°F. Cold flow properties could be a limitation to the use of B100 in the winter time. Some key properties in this regard are the cloud point and the pour point. The cloud point is the temperature at which wax formation can begin to plug the fuel filter. The pour point is a measure of the temperature at which the fuel is no longer pourable. Other than cloud point and pour point, cold filter plugging point, low temperature filterability, wax appearance point, and cold soak filterability are some other laboratory tests commonly used to define low temperature operability of biodiesel (Hoekman, 2009). The ASTM D6751 B100 standard does not include specifications for low temperature operability. However, the Cold Soak Filterability test, which determines the fuel filter blocking potential of biodiesel in cold condition, was included in the ASTM D6751 test method "Annex A1" in 2008.

Fuel quality is very important to owners of diesel engines. Consumers expect all fuels to meet certain minimum quality, safety, and performance standards and engine manufacturers expect a fuel quality that does not affect engine performance and durability. NREL has conducted several studies of the quality and stability of biodiesel and biodiesel blends in the US, dating back to 2004. Some of the early studies found failure rates were higher than should be expected, with between 15-59% of the samples failing to meet all of the ASTM D6751 specifications (McCormick et al., 2005; Alleman et al., 2007). A follow-up study in 2007 found significant differences in the quality levels between different producers (Alleman and McCormick, 2008). Large producers and BQ-9000 producers were found to hardly ever fail to meet the

specifications. Small and medium producers, however, still had significant failure rates, with approximately 30% of these samples failing oxidation stability. Studies of B20 quality by NREL has also shown examples of poor blending and mislabeling of pumps (McCormick et al., 2005; Alleman and McCormick, 2009; Alleman et al., 2010).

The biodiesel industry continues to strive to improve the product quality that is on the market. The biodiesel industry has established a cooperative and voluntary program for the accreditation of producers and marketers of biodiesel fuel called BQ-9000 that has improved the quality level of in-use biodiesel. The program is a combination of the ASTM standard for biodiesel, ASTM D6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices. BQ-9000 helps companies improve their fuel testing and greatly reduce any chance of producing or distributing poor quality fuel. To ensure that the fuel quality of biodiesel is acceptable for widespread use in California, it is suggested that a fuel monitoring program be implemented in California, with levels of stringency and enforcement similar to those for typical diesel fuel.

Fuel stability during storage and use is a major industry issue for diesel and biodiesel fuels as the oxidation products can plug up the fueling system and buildup deposits in the engine. An oxidation stability test (the Rancimat, ASTM - EN 14112 method) was added to the D6751 biodiesel specification in 2007. A recent study of biodiesel and biodiesel blend oxidation stability by McCormick et al. (2009) showed that B100 samples that do not contain a synthetic antioxidant will immediately begin to oxidize during storage. The study suggested that B100 should not be stored more than several months unless it is treated with synthetic antioxidant. McCormick's study also confirmed that the stability of B5 and B20 blends is mainly affected by the B100 stability, and is essentially independent of diesel fuel aromatic content, sulfur level, or stability. The antioxidant testing conducted in this study showed that commercial hindered phenolic antioxidants were very effective at preventing acid and insoluble formation during the storage of B100 and biodiesel blends. Other studies have found various oxidation additives to be effective including TBHQ (t-butyl hydroquinone), Ethyl Hitec 4733, pyrogallol (PY), and propyl gallate (PG) (Canakci et al., 1999; Waynick, 2005). Studies show that in many commercial systems, the fuel turnover rate is in a range (two to four months) where fuel stability with B100 has not been problematic. The ASTM D4625 data suggests that the least stable B100 could be stored for up to 8 months, while the most stable could be stored for a year or more. The National Biodiesel Board recommends a six month storage life for B100.

Biodiesel is very sensitive to microbial growth, and adding biocides to the biodiesel storage tank is a common method to control microbial contamination. Water contamination is another issue with biodiesel storage. Since water is more soluble in biodiesel than petroleum diesel, and water can promote microbial growth, water is undesired in the biodiesel (NREL, 2009). The use of a 10 micron filter at biodiesel fuel dispensers is an effective practice to prevent water entering the fuel tank and a 10 micron filter in the fueling system prevents water from entering the fuel injectors and engine system.

Biodiesel is currently being incorporated into California's diesel regulations in response to the low carbon fuel standard regulation. While biodiesel provides benefits in the emissions of many components, biodiesel does tend to increase NO_x emissions. While the magnitude of changes for

NO_x emissions can depend on a number of conditions, including load, operating conditions, and the base fuel against which biodiesel is being compared, the comprehensive California test program (Durbin et al., 2009a) appears to indicate that some form of NO_x mitigation will be required for biodiesel to ensure that the finished diesel fuel is NO_x neutral. The results from the California study also indicate that the magnitude of the NO_x increase will likely be greater for CARB-certified diesel fuels compared to diesel fuels used Federally, or in other states, that are subjected to less stringent regulations. As part of the California test program, several NO_x mitigation strategies were shown to be successful including additive formulations with di-tertiary butyl peroxide (DTBP) and formulations with about a 3 or 4 to 1 ratio of hydrogenated or GTL diesel compared to the biodiesel. While these formulations are viable, the development of more cost effective NO_x reduction strategies would provide a more economic path for the introduction of greater percentages of biodiesel.

4.3 Technical Limitations and Commercialization Gaps for Biodiesel

4.3.1 Biodiesel Feedstock Limitations

Feedstock availability is an important limitation to the expansion of biodiesel. There is enough virgin soy oil, recycled restaurant grease, and other feedstocks available in the US to produce ~1.7 billion gallons of biodiesel per year (AFAVDC, 2009c). This amount of biodiesel is ~5% of the US on-road diesel usage. The biodiesel industry is looking to expand its feedstock and production base beyond this level, however, in efforts to meet a larger percentage of the advanced non-cellulosic biofuels EISA requirements and to expand into the heating oil market.

Similar to the use of corn for fuel ethanol production, there has been concern expressed over the use of soybeans for fuel production because of the possible reduced availability of these crops for food products and the effect on the price of food goods if the price of soy increases. The impact of biodiesel on soybean agriculture is quite different from that of ethanol on corn farming. First, the amount of corn and soybean used for biofuel production is different. While 20% of the corn crop goes to ethanol production, only 3% of the soybean crop is used for biodiesel (USB, 2009). Second, biodiesel production uses the soybean oil, which is only 19% of the soybean, the rest of the solid soybean product can be utilized for livestock feed and human food.

Soybean oil is the major cooking oil and baking fats in the U.S. Today, 14% of the soybean oil is used for biodiesel. Soybean oil has many other competing uses, such as: human and animal food, soy milk and cheese, candles, soaps, cooking oil, flour, cosmetics, resins, plastics, inks, clothing, and vodka (Bloch 2008). Recycled grease also is used in soap production, oils, cosmetic and skin care products (North Carolina Department of Environment and Natural Resources 1999). A discussion of the impact of biodiesel production on soybean prices is provided below. Soybean prices also have an impact on production costs, which will be discussed in greater detail in section 4.3.2.

The soybean price can be impacted by a number of factors. Soybean and other food commodity prices increased dramatically between September 2007 and mid-2008, but have declined since then, as a result of the overall recession. Some of the factors that could impact soybean prices

include supply shortages, global food markets, higher energy prices, the declining US dollar, and/or speculation in commodity futures trading (Carter et al., 2008). Cross commodity linkages can also have an impact on soybean commodity prices, such as preferential planting of corn over soybeans.

Centrec Consulting Group, LLC, evaluated the impact of the biodiesel industry on the price of soybeans as part of a program sponsored by the United Soybean Board (Centrec, 2009a). This group found that the biodiesel industry's demand for soybean oil added up to \$0.10 - \$0.25 per-bushel to the price of soybeans. This provided U.S. soybean farmers an additional \$2.5 billion in net returns from 2005 to 2008. The study also found that the higher demand of soybean oil led to an increased supply of soybean meal, resulting in meal prices dropping by \$19 to \$45 per ton. This study does not mention the effect on prices of soy products used for human consumption. In a second study, Centrec (2009b) suggests that biodiesel prices will remain strongly tied to the price of diesel fuel, and that the relationship between biodiesel and diesel prices will likely set a new floor on soybean oil prices.

Other studies have suggested more significant impacts on biodiesel production on soybean prices. Wisner (2008) estimated that the price for soy for the 2007-2010 time period would range from \$10.15 to \$12.50 compared to estimated prices in the \$4.80 to \$5.30 range if the use of soybean oil was maintained at the same level as in 2004-2005. Carter et al. (2008) suggested that macroeconomic factors were likely responsible for this broader boom and bust of food commodity prices in 2007/2008, but that biofuel and trade policies in general continue to hold corn, soybean, and rice prices at approximately double their 2005 levels. These relationships are complex, however, as Carter et al. point out that the acreage used for corn increased by 19% in the 2007/2008 crop year, while the corresponding acreage for soybeans fell by 16%. Overall, it appears these higher estimates for increases in soybean prices could not likely be attributable to biodiesel production alone.

4.3.2 *Biodiesel Production Limitations*

FAME biodiesel production is a mature process and there is not much which can be done to improve the process, so the main limitation to biodiesel production is economic. The current biodiesel process configuration strongly ties the economic performance of a facility to the value of petroleum and the level of government incentives offered. This creates a large amount of commodity and policy risk, leading to the "boom and bust" cycles that have recently been witnessed in this market. Finding low cost feedstocks, expanding product offerings, and securing longer term incentives would improve the future economic prospects for the biodiesel industry.

Hoekman et al. (2009) noted that 80% of total biodiesel cost is attributed to feedstock. However, they do not present any specific feedstock costs. The cost of FAME from vegetable oils depends upon the cost to grow, harvest, and transport the vegetable source to the processing site and its value as a food crop. This chapter reviews several cost analyses of biodiesel production and the factors that most impact biodiesel production costs.

You et al. (2008) conducted an economic cost analysis of biodiesel production from soybean oil for biodiesel plants with processing capacities of 8,000; 30,000; and 100,000 tons/yr. For these three plant sizes, they estimated the total production costs as \$9,614,000, \$32,108,000, and

\$102,648,000/yr, respectively. The estimated cost of the soybeans was \$6,234,000, \$23,376,000, and \$77,920,000/yr, respectively. In this study, the soybean cost is 64.8%, 72.8%, and 75.9% of the total biodiesel cost. The authors concluded that the 100,000 ton/yr plant, i.e., the largest, was economically feasible.

Zhang et al. (2003) estimated the economics of an 8000 ton/yr biodiesel plant for four different processing options. The options were: (1) an alkali-catalyzed process to produce biodiesel from virgin vegetable oil, (2) an alkali-catalyzed process to produce biodiesel from waste cooking oil, (3) an acid-catalyzed process to produce biodiesel from waste cooking oil, and (4) similar to 3 except used hexane as an extraction solvent rather than water washing. The virgin vegetable oil used in this study was canola oil at a cost of \$500/ton while the waste cooking oil cost \$200/ton. For the four options, the total production costs were: \$7,590,000, \$7,760,000, \$5,920,000, and \$6,350,000/yr, respectively. The feedstock costs were: \$4,200,000, \$1,680,000, \$1,650,000, and \$1,650,000, respectively. In this study, the virgin canola oil is 55.3% of the total biodiesel cost and the waste oil is 21.6%, 27.9%, and 26.0% of the total biodiesel cost for cases 2, 3, and 4, respectively.

FAME production generates a 10 wt% glycerol byproduct (Johnson and Taconi, 2007). The expansion of FAME production from 2005 to 2009 has led to a glut of crude glycerol. Purified glycerol, or glycerin, is a high value product used in various foods, beverages, pharmaceuticals, cosmetics, and other personal care products. Because the crude glycerol from FAME production has many contaminants, such as alcohol, salts, heavy metals, and water, it is not economic to purify it for use in the above products. While it can be burned to produce thermal energy, the salts, heavy metals and water would still have to be removed, which makes this option uneconomic. Therefore, new value-added products of glycerol need to be developed to reduce this waste disposal problem, which is costly. Research is being conducted with conventional catalysts and biological conversion to convert the glycerol to valuable chemicals. There are also studies to produce hydrogen from glycerol (Byrd et al., 2008; Hisao Hori and Koike, 2005), and research in production processes that can produce a high purity glycerin (at least 98% pure) with no salt contamination (Bournay et al., 2005).

4.3.3 *Biodiesel Utilization Limitations*

For California, one of the most critical limitations with biodiesel use is the fact that it increases NO_x emissions. Although formulations can be developed with the use of additives or more paraffinic renewable diesel blends to neutralize any increases in NO_x emissions, such formulations have not been optimized for cost effectiveness. Biodiesel produced from feedstocks that are less prone to increasing NO_x emissions, such as those from animal tallow or yellow grease, could become more valuable in California since they could potentially be treated with lower additive rates or lower levels of renewable fuels.

While biodiesel has been developing as a transportation fuel, there are still some logistical barriers that can limit its expansion. Most diesel engine companies provide warranties up to at least a B5 level, but the extension of the warranties to B20 or higher depends on the specific engine and manufacturer. With the addition of new aftertreatment for the 2007 and 2010 model years, it is important to demonstrate that biodiesel will be fully compatible with these systems.

This would be an important step in increasing warranty coverage for all newer engines up to the B20 level.

The expansion of the biodiesel infrastructure could facilitate expansion of biodiesel. Currently, biodiesel is not fully integrated into the petroleum infrastructure. Biodiesel is not currently being transported through the existing pipeline network in the US. Biodiesel is typically splash blended instead of blending in-line as in traditional petroleum processes. Fuel tanks dedicated for biodiesel use are largely utilized for fleet applications, with more limited stations for biodiesel dispensing. Biodiesel dispensers have not as yet been UL certified for use. There are also issues with biodiesel utilization with the water board, with respect to tank leak regulations, and fire codes.

The use of biodiesel in pipelines is being evaluated by the biodiesel and pipeline industries in the US. In Europe, B5 has been run in pipelines for years already. The main issue with the use of biodiesel in the pipeline is its potential impacts on jet fuel. The aviation fuel community, including aircraft and engine manufacturers and petroleum supplier, has already formally approved the use of jet use containing up to 5 ppm of FAME, and the Federal Aviation Administration (FAA) has found that short term operation with up to 30 ppm in jet fuel does not pose a risk to flight safety (FAA, 2009). An industry working group is testing FAME in jet engine at levels up to 400 ppm, with a goal of getting approval for the use of up to 100 ppm in jet fuel. This group contains a wide variety of companies and organizations including, Boeing, Rolls-Royce, Green Earth Fuels, Exxon and the Kansas City Soybean Commission.

In the US, there have been several pipeline trials with biodiesel (McElroy, 2007; Northville Product Services and Colonial Pipeline, 2007; NBB, 2009c). In August 2006, a shipment of 75,000 barrels of B5 was transported from Houston to Linden, N.J., through a common-carrier pipeline operated by Colonial Pipeline. The base fuel specifications did not show any adverse impacts during this test, and it met all ASTM D 975 specifications, contained no water or sediment traces. Countrymark Co-op also conducted a 210,000 gallon B5 trial run in Indiana through a 238-mile company-owned pipeline in the summer of 2006 with similar positive results. Kinder Morgan conducted a test with 15,000 gallons of B5 in its plantation pipeline from Mississippi to Virginia in the spring of 2009. Taking into account the jet fuel testing and the existing pipeline experience with biodiesel, it appears that levels of B5 will likely be approved in the future for pipeline transport, although pipeline transport of higher levels of biodiesel would require additional study.

The unique fuel properties of biodiesel compared to diesel fuel also create some issues that at the very least must be considered, even though biodiesel is generally compatible with diesel engines. A key element for the successful implementation of biodiesel on a wide scale appears to be the quality of the fuel being utilized. The biodiesel industry has made significant progress in this area, but continued and ongoing improvement in this area is needed to reach quality levels typically required within the petroleum industry. If the fuel quality can be guaranteed to meet the D6751, it appears that other issues relating to filter clogging, materials compatibility, and cold temperature operation can be addressed with appropriate caution and good fuel management practices. With the introduction of an ASTM standard for B5-B20, it will also likely be easier to address engine manufacturer concerns with respect to warranty issues. While most of these

utilization issues can be addressed with time, the inability to use biodiesel in the existing pipeline structure will be a long term liability that could become a more significant disadvantage as more fungible fuels continue to be developed.

4.4 Environmental and Other Considerations

Although biodiesel has generally been shown to reduce many of the primary emissions, including THC, CO, and PM, there is also a potential increase in NO_x that must be considered from an environmental standpoint. The U.S. EPA conducted an analysis of the impacts of biodiesel on emissions in the 2002 timeframe (US EPA, 2002). Based on their statistical analyses from a range of different studies, the EPA found that NO_x increased on average by approximately 2% relative to the base case scenario diesel and by 5.1% relative to a clean diesel more similar to the properties of diesel fuel in California. In a subsequent study, McCormick et al. (2006) argued that a more comprehensive examination of the biodiesel engine and chassis dynamometer testing indicates that B20 does not have a significant impact on NO_x. They included an evaluation of chassis dynamometer studies included in EPA's comprehensive report and studies conducted since the time of EPA's report. Hoekman et al. (2009) conducted a more comprehensive assessment of the available literature on biodiesel NO_x emissions and concluded that NO_x increases only 2-3% in going from pure diesel to 100% biodiesel and that there is no change at 20% (B20) biodiesel. CARB in conjunction with the University of California at Riverside and the University of California at Davis is in the process of evaluating the issue of biodiesel NO_x emissions as part of the implementation of its LCFS program. Engine testing has been conducted on a 2006 Cummins ISM 370 and a 2007 MBE4000 engine using CARB low sulfur diesel and blends of soy, animal fat, renewable, and GTL diesel up to 100% as part of this study (Durbin et al., 2009a). The results of these engine tests have indicated that NO_x emissions increase with increasing biodiesel level for nearly all testing conditions. The results are generally more consistent with the EPA estimates for using biodiesel in "clean" diesel fuel, although there are differences between the NO_x increases for a soy-base and an animal-based biodiesel.

CARB's (CARB, 2009b, 2010) Well to Wheel (WTW) GHG emissions for various scenarios of biodiesel production using the CA-GREET version 1.8b are provided in Table 4-2. The results show that the biodiesel produced from the conversion of waste oils would provide significant reductions in carbon intensity values. The carbon intensity values for biodiesel produced by the conversion of soybeans to biodiesel provide some benefits in carbon intensity relative to the baseline diesel, but the benefit is much smaller due to the assessed land use effects.

Table 4-2: Adjusted Carbon Intensity Values for Diesel Fuel and Biodiesel.

Fuel	Pathway Description	Carbon Intensity Values (gCO _{2e} /MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Diesel	ULSD – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	94.71	0	94.71
Biodiesel	Conversion of waste oils (Used Cooking Oil) to biodiesel (fatty acid methyl esters -FAME) where “cooking” is required	15.84	0	15.84
	Conversion of waste oils (Used Cooking Oil) to biodiesel (fatty acid methyl esters -FAME) where “cooking” is not required	11.76	0	11.76
	Conversion of Midwest soybeans to biodiesel (fatty acid methyl esters -FAME)	21.25	62	83.25

Hoekman et al. (2009) reviewed 24 studies of the relative Global Warming Potential (GWP) of biodistillates versus conventional diesel fuel and found the GWP of the biodistillates were 10 to 90% lower than from conventional diesel fuel. However, if high N₂O emissions, from fertilizer application, are assumed then the biodistillates have a higher GWP than conventional diesel fuels.

4.5 Ongoing Research

The limitations to the expansion of biodiesel are primarily found in the area of feedstocks and in barriers to utilization of biodiesel. This is where most of the ongoing research is focused, although some research into improved production is also being conducted.

4.5.1 Ongoing Biodiesel Feedstock Research

The feedstock used has a large impact on the economics and environmental profile of the finished biodiesel. The price for the most widely used oils, derived from soybeans and rapeseed, has climbed along with the demand for biodiesel. In addition, the demand for some of the highest oil yielding sources, such as oil palms, has led to deforestation and an increase in the use of fertilizers in Southeast Asia. These issues have pushed biodiesel producers to look for other sources of oils that can be produced at low cost without causing significant environmental damage.

Sanford et al. (2009) studied a variety of feedstocks to evaluate the impact their properties would have on production and processing requirements. Biodiesel is produced via a transesterification process where fats or oils are reacted with methanol to produce methylesters (the biodiesel component) with glycerol as a byproduct. The properties of the feedstock influence the production and processing requirements. For instance, if a feedstock has greater than 0.050 wt% water then it needs to be dried to minimize effects from emulsions during transesterification. If a feedstock has greater than 0.5 wt% free fatty acid (FFA) then it has to be esterified before being transesterified. If a feedstock has greater than 10 ppm phosphorus or greater than 5 ppm calcium and magnesium it has to be pretreated with phosphoric acid and dried before being

transesterified. Any pretreatment adds production costs so just having a feedstock that can be grown and sold at a low cost doesn't guarantee lowering the cost of the biodiesel.

Sanford, et al. (2009) evaluated 36 biodiesel feedstocks and produced laboratory quantities of biodiesel from 34 of them. The properties of the feedstocks and the biodiesel were determined. In the Sanford et al. study, 21 of the 36 feedstocks had a water content exceeding 0.050 wt%, 19 out of 36 had greater than 10 ppm phosphorus, 15 out of 36 had greater than 5 ppm calcium, 10 out of 36 had greater than 5 ppm magnesium, and 18 out of 35 feedstocks had FFA in excess of 0.5 wt%. Just considering these 5 factors, 26 out of the 36 feedstocks would require some sort of pretreatment.

The pretreatment process requirements depend on the properties that must be brought into specifications. Lowering the water content below 0.050 wt% involves drying the feedstock using heat and vacuum. To lower calcium, magnesium, and/or phosphorous below 5 ppm, 5 ppm, and 10 ppm, respectively, 4 processes employing several chemicals are used. The processes are: heating and high shear mixing in 85% phosphoric acid, followed by neutralization and washing, centrifuging, and bleaching, drying, and filtration. The FFA is lowered (esterified) by heating a mixture of feedstock, activated Amberlyst BD catalyst, and dry methanol to reflux for a period of time, then removing the methanol by vacuum. If the feedstock has >0.5 wt% FFA and calcium or magnesium exceeds 5 ppm or the phosphorous exceeds 10 ppm the feedstock has to be pretreated with phosphoric acid before being esterified. Of the 20 feedstocks which had a high FFA content, six of them required repeating the esterification process one time. The Karanja oil required repeating the esterification seven times, and even then the FFA content was greater than 0.5 wt%. Clearly, the esterification and phosphoric acid pretreatment can add considerable capital and operational costs to biodiesel production from feedstocks requiring either or both of these pretreatments.

Jatropha is one feedstock which has been high on the list for replacing soybeans because it is a bush of little commercial importance that can potentially grow on marginal soils. The general thought has been that biodiesel producers that can handle low quality feedstocks, such as Jatropha, will have an economic advantage over other producers. However, the Sanford et al. study indicated that Jatropha oil had to be pretreated to reduce water content, FFA, phosphorus, calcium, and magnesium. The additional capital investment for pretreatment, plus the operating costs and the disposal costs for the wastes from the pretreatments, could more than offset a very low feedstock cost.

Sanford et al. also made laboratory quantities of biodiesel B100 for each of the feedstocks and measured properties contained in ASTM standard D6751 for B100. The majority of the B100's passed nearly all the specifications. There were 6 feedstocks that yielded a B100 which failed to meet 3 or more of the ASTM D6751 specifications, however, indicating that more processing was needed for those feedstocks.

Basha et al. (2009) reviewed literature reports on biodiesel production, combustion, emissions and performance. They identified more than 350 oil-bearing crops as possible sources for alternative fuels for diesel engines, but concluded that only a few have potential for biodiesel production, like sunflower, rapeseed, palm and Jatropha. They do not state why they cite only

these four as potential sources or why soy is left out of the list. They also note that the NO_x emissions are higher for all the biodiesel blends compared to petroleum diesel.

4.5.2 *Ongoing Biodiesel Production Research*

Recently, a technique to synthesize esters using oxygen-coated gold nanoparticles was published (Urquhart, 2009; Xu et al., 2009). The advantages of this method are that it is highly selective (i.e., specific esters can be targeted for production); the reactions occur at low temperature, the reactions occur entirely on the surface of the gold catalyst instead of in the solution phase, and the production of environmental pollutants is minimized. Considerable work remains to determine if the method can be scaled up for practical use.

An alternative production method for FAME has also been proposed which produces nearly the theoretical yield of FAME and a high purity glycerin (at least 98%) with no salt contamination (Bournay et al., 2005). The traditional methods use homogeneous basic catalysts which lead to waste products after neutralization with mineral acids. Bournay et al. (2005) use a continuous production process with a heterogeneous catalyst. The process doesn't require catalyst recovery nor aqueous treatment steps and thus the product purification steps are much more simplified. The glycerin is directly produced and is exempt from any salt contamination.

4.5.3 *Ongoing Biodiesel Utilization Research*

Biodiesel is currently being incorporated into California's diesel regulations in response to the low carbon fuel standard regulation. While biodiesel provides benefits in the emissions of many components, biodiesel does tend to increase NO_x emissions. While the magnitude of changes for NO_x emissions can depend on a number of conditions, including load, operating conditions, and the base fuel against which biodiesel is being compared to, the comprehensive California study appears to indicate that some form of NO_x mitigation formulation will be required along with biodiesel blends to ensure that the finished blend will be NO_x neutral (Durbin, et al., 2009a). The results from the California study also indicate that the magnitude of the NO_x increase will likely be greater for CARB-certified diesel fuels compared to diesel fuels used federally or in other states that are subjected to less stringent regulations. As part of the California program, several NO_x mitigation strategies were shown to be successful for specific engines including additive formulations with di-tertiary butyl peroxide (DTBP) and formulations with about a 3 or 4 to 1 ratio of hydrogenated or GTL diesel compared to the biodiesel. While these formulations are viable, the development of more cost effective NO_x reduction strategies would provide a more economic path for the introduction of greater percentages of biodiesel.

Krahl, et al. (2009) studied the mutagenicity of particulate matter and condensates from the combustion of biodiesel, vegetable oil, gas-to-liquid, and petrodiesel fuels. Mutagenicity is a measure of the capacity of a physical or chemical agent to induce or increase the frequency of mutation in an organism. This is an important measure since mutations can trigger adverse health effects such as cancer. They found that the mutagenicity of rapeseed oil was 5.4 to 9.7 times greater than petrodiesel, and that rapeseed methyl ester was moderately higher than petrodiesel. The gas-to-liquid mutagenicity did not differ significantly from petrodiesel. Regulated emissions,

with the exception of NO_x which had up to 15% higher emissions than petrodiesel, were lower than petrodiesel.

As part of a comprehensive assessment of emissions from the use of biodiesel, CE-CERT will send samples to the University of California, Davis for evaluation of the toxicity of the exhaust (Durbin et al., 2008). The planned toxicity testing is shown in Table 4-4.

Table 4-3: Planned Toxicity Testing of Biodiesel Exhaust Emissions

Biological Test	Sampling Method	Bioassay/biological Assay	Sampling schedule	Vehicle Test Cycle
Mutagenicity	Filter/PUF	TA98 ± S9 TA100 ± S9 TA102 (selected samples) TA104 (selected samples)	In-depth	UDDS
DNA damage	Filters	Comet assay	In-depth	UDDS
Oxidative stress and inflammation	Filters	Human lung and macrophage assays: Inflammatory cytokines: IL-8 & TNF Prostaglandin synthase COX-2 Heme oxygenase-1 HO-1 C reactive protein	In-depth	UDDS

4.6 Recommendations for Biodiesel Research

Biodiesel use has grown considerably over the last 10 years and the industry has reached some level of maturity. From a conversion standpoint, there is little that can be done to improve the performance of the FAME process. The yields and quality of the finished product are already quite high, and any improvements would be small. From a utilization standpoint, biodiesel can be utilized in existing diesel vehicles and a distribution network and some infrastructure has already been developed. Potentially, there are some issues with the use of biodiesel, including long term durability of systems with biodiesel, engine warranties, fuel quality, storage stability, and cold weather operability. While these issues are relevant for continued expansion of biodiesel, there are a number of other research organizations involved in addressing these issues, and it is not likely that further funding in these areas would greatly improve the commercialization prospects of biodiesel. The inability to transport biodiesel via a pipeline is also an issue.

The development of greater value finished products or byproducts could provide economic benefits for biodiesel use. Supply of the major co-product from biodiesel production, crude glycerin, has grown much faster than demand. This has greatly depressed prices, and reduced this potential source of revenue for biodiesel producers. Typical uses of glycerin have included pharmaceuticals, personal care products, and resins. In an effort to increase glycerin demand, exploration has been made into using glycerin as a boiler fuel and as animal feed. Greater

demand for crude glycerin or improvements in the quality of glycerin produced would improve the overall biodiesel production economics. Expanding the products that could be made from biodiesel or finding niche opportunities for product use (for example, as a feedstock for chemicals production) could also improve the economics and add flexibility to the process. While this area has some potential benefits for the biodiesel industry, there are already some ongoing efforts in this area within the industry, and it is not likely that further funds would provide a significant benefit to expanded commercialization.

In the near term, the development of biodiesel formulations that are neutral with respect to NO_x formation will be important. This is particularly important in California, where regulations prohibit “backsliding” for any specific emissions component. The NO_x mitigation formulations being proposed from the comprehensive California program are relatively expensive in terms of the additive levels needed or the need to co-blend higher levels of renewable diesel to a level where it would nearly eliminate the need for the biodiesel. The demonstration of more effective additives at lower dose rates would provide greater flexibility in meeting the low carbon fuel standard levels. Another strategy would be to emphasize biodiesel feedstocks, such as animal-based biodiesel, that would be less conducive to increasing NO_x emissions.

The development and expansion of new feedstocks could also be important, since this is probably the most important factor in the production costs. Research into new biodiesel feedstocks would also be of value to the hydrogenated vegetable oil process, discussed in chapter 8. The new feedstocks would need to be produced at low cost, not require expensive pretreatment, and have a minimal impact on the environment, such as through deforestation or increased fertilizer use. For example, interest in oils produced from *Jatropha*, a bush of little commercial importance that can potentially grow in marginal soils, has grown. It might also be possible to develop feedstocks with unique fatty acid profiles that would be more favorable for use in fuels, such as improved cold weather properties. The development of feedstocks with a reduced tendency for increasing NO_x emissions would also be valuable. The properties of any new potential feedstocks need to be determined, including the overall composition, moisture levels, free fatty acids (FFAs), and other impurities. This information will provide an indication as to whether more extensive/expensive pretreatment will be needed for processing. The finished biodiesel product from any new feedstock would also have to be characterized to ensure that the product can readily meet all the ASTM D6751 specifications. It may also be worthwhile to investigate the potential of lower quality or more readily available feedstocks that may require more extensive pretreatment and associated capital investment for processing, but may still offer some economic advantages.

Although biodiesel is a relatively mature and proven alternative fuel, it is suggested that some PIER funds be spent in this area, particularly for alternative feedstocks. The two most promising areas of research appear to be in the development of feedstocks and NO_x mitigation strategies. The development of more cost effective NO_x mitigation strategies would be more critical in the near term, as biodiesel is being introduced into the marketplace. Research in the feedstocks area would be more helpful to stabilize the production costs over the longer term, as well as providing producers potentially more flexibility in the short term. Feedstock research would also provide benefits to other production technologies, such as hydrogenated renewable diesel, which would provide broader implications for such research. There are also more practical issues that will continue to need to be addressed by the biodiesel industry, such as fuel tank infrastructure,

vehicle compatibility issues, and continued improvements in fuel quality, but it is not likely any significant breakthroughs, such as those targeted for PIER research, will occur in these areas.

5 Biochemical-Based Cellulosic Fuels

5.1 Introduction

While conventional ethanol processes rely on feedstocks that contain high levels of sugars or starches, significant efforts are underway to develop ethanol production processes that are able to derive ethanol from cellulosic feedstocks. These cellulosic feedstocks would include woody biomass and agricultural residues such as corn stover and wheat straw. In comparison with ethanol made from more traditional sources like corn starch and cane sugars, cellulosic ethanol can be produced from a much more abundant and diverse mixture of source materials that can be low in cost. On the other hand, the processing requirements to convert lignocellulosics to sugars which can be fermented to ethanol are greater than those needed to produce ethanol via fermentation from more traditional sources. The processes to convert cellulosic feedstocks can be divided into two categories: biochemical pathways and thermochemical pathways. The biochemical pathway entails pretreatment of the feedstock, hydrolysis of the feedstock, followed by fermentation processes. The thermochemical pathway involves gasification of the feedstock to produce syngas, followed by the catalytic conversion of the syngas to alcohols such as methanol and ethanol. In this chapter, the technical development and ongoing research for biochemical-based cellulosic transportation fuels are reviewed, their technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for cellulosic biochemical fuels are provided. This chapter largely focuses on the production of cellulosic ethanol via biochemical processes, but also covers biochemical processes used for the production of other fuels. The corresponding evaluation of the thermochemical processes are provided in chapters 6-8.

5.2 Development of Biochemical-Based Cellulosic Processes for Transportation Fuels

5.2.1 *Biochemical-Based Cellulosic Process Feedstocks*

One of the most important attributes with the use of cellulosic ethanol is the potential to use a much wider range of feedstocks than conventional ethanol, thus providing an opportunity to achieve alternative fuel use levels that cannot be achieved simply through food crops. According to the Alternative Fuels & Advanced Vehicles Data Center (AFAVDC, 2009d), cellulosic feedstocks suited to ethanol production include the following:

- Agricultural residue—crop residues such as wheat straw and corn stalks, leaves, and husks;
- Forestry residue—logging and mill residues such as wood chips, sawdust, and pulping liquor;
- Dedicated energy crops—hardy, fast-growing grasses such as switchgrass and miscanthus etc. grown specifically for ethanol production;
- Municipal and other wastes—plant-derived wastes such as household garbage, paper products, paper pulp, and food-processing waste;
- Trees—fast-growing trees such as poplar and willow grown specifically for ethanol production.

These products have many advantages over starch- and sugar-based feedstocks:

- They are more abundant and thus can produce a larger volume of ethanol;
- They are waste products, or can be grown specifically for ethanol production;
- They can be grown on marginal land not suitable for other crops;
- They require less fossil energy to grow/collect them and convert them to ethanol;
- They are not human food products.

As mentioned previously, crops which would be grown exclusively for fuel production are called “energy crops”. For energy crops, switchgrass is one of the preferred species because it is a native “well-behaved” perennial grass which develops “a deep, vigorous root system to acquire nutrients and water under diverse soil and climate conditions.” If substantial quantities of such crops are removed annually then nitrogen fertilization will be required to maintain adequate yields. Other grasses that have received consideration as energy crops for ethanol production are: Big Bluestem Genotype, Forage Sorghum, Sericea Lespedeza Serala, Sweet Sorghum, Tall Fescue (AVAVDC, 2009d), Giant Miscanthus, Eastern Gammagrass Busby et al. (2007) and burmudagrass, weeping lovegrass, and flaccidgrass Haque et al. (2008).

The newly established bioenergy research centers have made tremendous efforts to cultivate “superior” energy crops that are more suitable to cellulosic ethanol production (DOE, 2009e). For example, the BioEnergy Science Center (BESC) focuses on genetic modification of switchgrass and poplar to alter the biochemistry of plant cell-wall biosynthesis to develop varieties that are easier to break down into fermentable sugars. While at the Joint BioEnergy Institute (JBEI), researchers are investigating metabolic pathways involved in lignin biosynthesis and developing plants that can be deconstructed more easily. Their focuses are rice (a model grass) and Arabidopsis (a model tree). Great Lakes Bioenergy Research Center (GLBRC) uses information from model and agronomic systems to breed plants (cornstalks and switchgrass) with increased energy density and digestibility. It is expected that these efforts in the near future will lead to a great impact on the development of feedstocks well tailored to cellulosic ethanol conversion.

The US Energy and Security Act of 2007 (EISA, 2007) specifies that by 2022 the US is to produce 36 billion gallons of renewable fuels, 15 billion from conventional starch-based biofuel and 21 from advanced technologies. Of the 21 billion gallons, 16 billion are to be cellulosic ethanol. Kumarappan et al. (2009) estimated the feedstock requirements for 3 production targets, as shown in Table 5-1. Assuming a conversion rate of 70 gals/bdmt, it would require 300 million bdmt of biomass to produce 21 billion gallons. Based upon Table 2-1 this quantity could be available at a price below \$50/bdmt.

Table 5-1: Biomass Feedstock Requirements and Expected Composition to meet Cellulosic Ethanol Production Targets in the US

<i>Ethanol production target billion gal (@70 gal/bdmt)</i>	<i>7</i>	<i>14</i>	<i>21</i>
Required biomass (million bdmt)	100	200	300
Agricultural Residues	67.3	147.0	180.0
Energy crops	-	-	9.0
Forest and Mill Residues	12.0	22.0	80.0
MSW	20.7	31.0	31.0

Towards the 21 billion gals of cellulosic ethanol required in 2022, Kumarappan et al. (2009) estimate California could produce 415.8 million gals. They estimate the biomass source for this California production would be agricultural residues (920,000 mbdmt/yr = 64.4 million gals) and forest and mill residues (5,020,000 mbdmt/yr = 351.4 million gals).

Figure 5-1 presents the estimated dry tonnage of biomass feedstock, primarily for ethanol production, potentially available in the United States (AFAVDC –2009d). The total estimated potential is 1.36 billion bdmt/yr. This information is from Perlack et al. (2005) and is based upon a high crop yield increase and land use change. The figure is divided into non-agriculture sources (top half) and agriculture sources (bottom half). Nearly all of the ~3 fold increase in total biomass represented in this figure, relative to currently estimated biomass feedstock (see Table 2-4), is from the assumption of increased crop yield and land use change. If all of this production is realized, and if it can be converted to ethanol with a yield of 70 gal/bdmt, then it would produce 95.5 billion gallons of ethanol. While these resources are distributed throughout the United States, the highest concentrations are in the Midwest, Southeast, and Northwest.

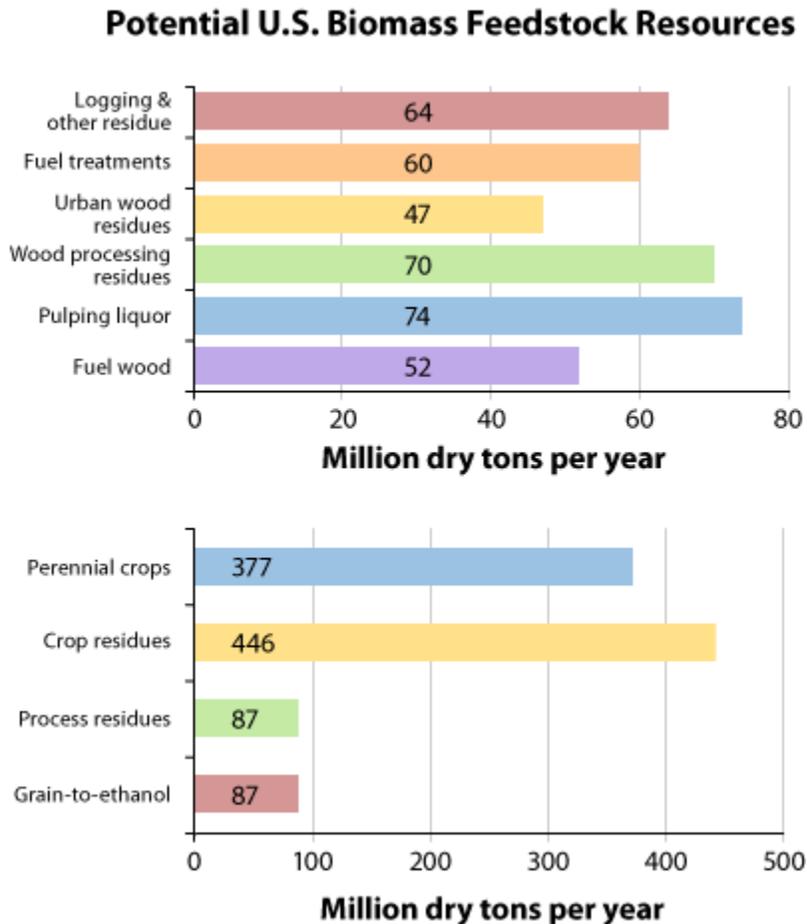


Figure 5-1: Estimated National Biomass Feedstock Resources

Within California the highest potential production of biomass (>500,000 tons/yr/county) are in counties north of San Francisco and is primarily from Forest and Primary Mill Residues. The

potential production in most of the rest of the state is between 0 and 100,000 tons/yr/county with small pockets with production potentials between 100,000 and 500,000 tons/yr/county.

Hague et al. (2008) note that while cellulosic biorefineries are initially expected to use crop residues, wood residues, and other waste products as feedstocks, that dedicated energy crops will be required to achieve long-term policy goals. It could require more than 50 million US acres of cropland, idle cropland, and cropland pasture to grow energy crops such as switchgrass.

5.2.2 *Biochemical-Based Cellulosic Production Processes*

Currently, there are two primary conversion pathways from cellulosic biomass to fuels: thermochemical and biochemical. For the thermochemical route, heat is applied to convert solid biomass into gaseous/liquid intermediates that can be reliably converted to liquid fuels. In contrast, biochemical conversion utilizes organisms to convert cellulosic biomass to fuels and chemicals. Biochemical ethanol production processes initially separate the biomass into its main constituents: cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are the “main building blocks” of biomass materials, while lignin is the “glue” that holds the cellulose and hemicellulose together. Biochemical ethanol production incorporates two main stages: hydrolysis of polymeric carbohydrates to short chained fermentable sugars, and metabolic conversion of those sugars to products. The breakdown of cellulosic biomass to sugars during hydrolysis is slow as a result of the natural resistance or recalcitrance developed by plants to biological degradation. The slow rates for this breakdown process are a barrier to the commercialization of biological conversion processes. To make biochemical ethanol production more commercially viable, sugar release rates must be increased by an order of magnitude or more over those found in nature. Traditionally, concentrated acid or two-stage dilute acid hydrolysis has been employed to hydrolyze cellulose and hemicellulose into its monomeric sugars. Enzymatic hydrolysis has many advantages over these other hydrolysis methods, however, and has been the primary focus of research efforts in this area. These advantages include milder reaction conditions, less sugar degradation, and the use of a biological catalyst.

Biochemical processes utilize enzymatic hydrolysis typically employ a pre-treatment process to accelerate the separation process. The objective of this pre-treatment is to alter or remove structural and compositional factors present in plant biomass that hinder the hydrolysis of the organic material (Mosier 2007). These pre-treatment processes have not been widely demonstrated at commercial scales, although efforts are underway to do so. Common pre-treatment processes include:

- Dilute Acid
- Hot Water
- Continuous Steam Explosion
- Ammonia Fiber Explosion (AFEX)
- Ammonia Recycle Percolation (ARP)
- Lime

For enzymatic hydrolysis, following pre-treatment, the cellulose and hemicellulose are hydrolyzed into fermentable sugars by a combination of cellulases and hemicellulases enzymes,

which are protein catalysts accelerating the hydrolysis reaction. Typical enzymatic hydrolysis requires hours to days depending upon the method of pre-treatment and enzyme loading. The hydrolysis of cellulose and hemicellulose results in the presence of both 5- and 6-carbon sugars, which are fermented into alcohols by organisms, i.e., yeast. These alcohols are distilled to obtain the purity of ethanol in a process similar to that of a first generation ethanol process.

It is important to note that while first generation ethanol production from starch-based crops relies on the fermentation of glucose, a 6-carbon (C6) sugar, the hydrolysis of cellulose yields a variety of sugars, including 5-carbon (C5) sugars such as xylose and arabinose, as well as other C6 sugars. The yeasts currently used in first generation ethanol processes are not able to efficiently ferment these compounds. In addition, the solution that results from the pretreatment and hydrolysis of the biomass feedstock, also known as the hydrolyzate, contains compounds such as acetic acid that can prove toxic to microorganisms. Developing microorganisms that can convert a variety of sugars and thrive in the hot hydrolyzate environment has been a focus area of recent research associated with the production of ethanol from cellulosic biomass. Public/private research partnerships have been established to develop both yeasts and bacteria that are capable of converting C5 and C6 sugars to ethanol with increasing efficiency.

While several companies are working to develop commercial-scale biochemical ethanol production facilities, there are no such facilities currently in operation in the United States. Each of these companies is developing proprietary processes that will employ novel enzymes and microorganisms to facilitate the production of ethanol from cellulosic feedstocks. Some of the key companies working to develop commercial-scale facilities include:

- Abengoa Bioenergy (Abengoa, 2010)
- BlueFire Ethanol (Bluefire, 2010)
- Iogen (Iogen, 2010)
- Mascoma (Mascoma, 2010)
- POET (POET, 2010)

5.2.2.1 Abengoa Bioenergy

Abengoa is a global technology company with a primary focus on sustainable development. Abengoa owns and operates several conventional ethanol production plants in Europe and the United States. They are actively developing enzymatic hydrolysis ethanol production facilities, employing pre-treatment process technology developed by SunOpta BioProcess Group.

Abengoa is currently operating an enzymatic hydrolysis pilot facility in York, Nebraska. The pilot facility began operation in 2007, with the capability to process up to 1.5 tonnes of biomass per day. In 2005, Abengoa began construction of a 5 million liter per year (1.3 MGY) demonstration facility located at the company's BCyl Cereal Ethanol Plant in Spain. This facility, currently being commissioned, will use agricultural residues (primarily wheat and barley straw) as feedstock.

Abengoa is also developing an advanced biorefinery to be located in Hugoton, Kansas. The company refers to this project as the Abengoa Bioenergy Hybrid of Kansas (ABHK).

Construction of this project is scheduled to begin in 2010, with commercial operation anticipated in early 2012. Abengoa estimates that the facility will have a capital cost greater than \$450 million. To offset a portion of these costs, the U.S. Department of Energy (U.S. DOE) has awarded the company \$76 million for the project. The facility is expected to produce 16 million gallons of ethanol annually from enzymatic hydrolysis processes. Abengoa intends to utilize a variety of feedstocks, including corn stover, wheat straw, milo stubble, and switchgrass. A key feature of ABHK is the integration of a biomass-fired gasification plant, which will generate syngas that may be combusted to produce process steam and electricity, with excess electricity provided to the grid. According to Abengoa, the facility may provide up to 70 MW of renewable power (Abengoa, 2009a). In the future, Abengoa intends to develop syngas-to-ethanol processes that may be used to generate additional ethanol (Abengoa, 2009b).

5.2.2.2 BlueFire Ethanol

Based in Irvine, California, BlueFire Ethanol employs the Arkenol concentrated acid hydrolysis process to produce ethanol from a wide variety of feedstocks. BlueFire's primary business strategy involves using cellulosic waste materials from municipal sources to create fuel grade ethanol. The feedstock for this process must be cleaned and ground to a particle size of less than 10mm. A moisture content of 10% is expected, but drying may be necessary since excess moisture can degrade the concentrated acid hydrolysis process. This very specific feedstock requirement raises the feedstock cost relative to other cellulosic ethanol routes. After the waste is sorted and prepared, concentrated sulfuric acid is used to break down the cellulose and hemicellulose into fermentable sugars at a temperature of 35-65°C. Following this, solids are removed and sent to a second reactor where more acid is added at a temperature of 80-100°C. Lignin and other solids are removed and a membrane separation process is used to separate the acid from the fermentable sugars. The lignin can be used to produce steam and electricity. Following acid recovery, the sugars are fermented and the impurities are removed.

BlueFire currently has plans to develop two facilities in the United States. The first facility, located in Lancaster, California, will produce 3.7 MGY of ethanol derived from "green wastes" (i.e., wood chips, grass cuttings and other organic wastes). The company is also working to develop an 18 MGY ethanol production facility in Fulton, Mississippi. Originally slated to be located in California, the U.S. DOE has provided more than \$80 million in funding to assist in this development (Bluefire, 2009). While the Lancaster facility is expected to be operational by the end of 2011, BlueFire has not announced when the Fulton facility is likely to begin production of waste-derived ethanol.

5.2.2.3 Iogen

Iogen is a Canadian biotechnology firm that manufactures enzymes for the pulp and paper, textile, and animal feed industries. The cellulosic ethanol process developed by Iogen employs a multistage hydrolysis process that separates the saccharification and fermentation steps. The company produces enzymes for the treatment process and claims that yields greater than 80 gallons per ton of fiber (greater than 25 percent by mass) are achievable. Biomass is pre-treated with dilute sulfuric acid, and then undergoes steam explosion to increase the surface area for the

enzymes to act upon. The lignin removed from the biomass is used to fuel the process and create additional electricity.

Iogen has partnered with Royal Dutch Shell (Shell is a 50 percent equity partner in the company) and has also received investments from Goldman Sachs. Iogen is currently operating its demonstration-scale facility located in Ottawa, Ontario. This facility utilizes wheat straw as a feedstock to produce 40,000 liters of ethanol per month (roughly 0.13 MGY), and Iogen claims that its fuel is the first cellulosic ethanol product to be blended with gasoline and sold commercially (Iogen, 2009).

While Iogen was awarded funding (up to \$80 million) in February of 2007 from the U.S. DOE for the development of a commercial-scale facility in Idaho, the company confirmed in mid-2008 that it has suspended those efforts in favor of developing a similar facility in Saskatchewan (CNEWS 2009). No timetable for the development of the Saskatchewan facility has been announced.

5.2.2.4 Mascoma

Established in 2005, Mascoma is focused on the development of advanced pre-treatment and enzymatic hydrolysis processes. In May of 2009, Mascoma announced that the company has achieved a significant breakthrough in the development of a single microorganism capable of (1) producing both the enzymes required for the hydrolysis of cellulosic materials and (2) fermenting cellulose-derived sugars into ethanol (Mascoma, 2009). Mascoma claims that its proprietary organism can produce both products “at high yield in a single step.” The production of cellulase enzymes is one of the larger operating costs associated with cellulosic processes. The utilization of a single microorganism for the production of both cellulase enzymes and ethanol, which Mascoma refers to as consolidated bioprocessing (CBP), is expected to significantly reduce the production costs for the Mascoma process.

Mascoma is currently producing ethanol from cellulosic feedstocks at its pilot facility in Rome, New York. Under its subsidiary, Frontier Renewable Resources, the company is developing a commercial-scale facility in Kinross, Michigan that will produce 20 MGY of cellulose-derived ethanol. At present, Mascoma anticipates that the Kinross facility will be commissioned in the fall of 2012.

5.2.2.5 POET

POET, formerly known as the Broin Companies, is one of the leading conventional ethanol producers in the United States. The company is developing enzymatic hydrolysis ethanol production technologies with partners including DuPont and Novozymes. The company claims that its proprietary BFrac™ advanced corn fractionation process and its proprietary BPX™ process, which POET describes as a “raw starch hydrolysis” process, will be employed in the cellulose-to-ethanol process. No additional information regarding the process is known. In November of 2008, POET achieved pilot-scale production of cellulosic ethanol at its Scotland, South Dakota research facility.

In 2007, POET was awarded funding from the U.S. DOE for up to \$80 million (limited to 40 percent of the total capital cost of the facility) for a biorefinery expansion project in Emmetsburg, Iowa. The existing dry mill facility produces 50 million gallons of ethanol per year. When completed in 2011, the expanded facility will produce a total of 125 million gallons per year of ethanol. One-fifth of the total ethanol produced (25 million gallons per year) will come from the cellulosic ethanol process. Corn cobs will be the primary fuel for the cellulosic process. In October of 2008, POET announced that the U.S. DOE would provide the full \$80 million award to the company. The state of Iowa has also awarded \$15 million to the company to assist with the development of the project.

A recent press release from POET announced that the company has achieved significant cost reductions in its cellulosic process over the past year. According to this press release, “[r]eductions in energy usage, enzyme costs, raw material requirements and capital expenses have reduced POET’s per gallon cost from \$4.13 to \$2.35 over the course of the past year, and the company’s goal is to be below \$2 by commercial plant start-up.” (POET, 2009)

These companies, and others including DuPont, Danisco and Verenum, intend to commission commercial-scale facilities ranging in size from 15 to 25 MGY in the next 2 to 5 years. While each will employ proprietary variations, these facilities will utilize agricultural residues (Abengoa, Iogen, Mascoma, and POET) or green wastes (BlueFire) that must be enzymatically hydrolyzed and fermented. It is likely that financial strength and the ability to manage the construction and commissioning of initial facilities will determine, in part, the eventual commercial success of these companies. However, from a technical perspective, the success or failure of each of these companies is likely dependent upon the performance of their proprietary enzymes and microorganisms relative to those of their competitors.

5.2.2.6 Other Biochemical Processes for the Production of Fuels

There is some ongoing research in the use of biochemical processes in the production of biodiesel. Menon & Associates was awarded an \$800,000 grant from the California Energy Commission to convert California almond husks and grape pulp into a feed stock for biodiesel via a bacterial pathway (Randolph, 2009). The Sorrento Valley company, which is putting up \$500,000 of its own money towards the three-year program, plans to convert the pulp, known as "cellulosic waste," into an oil-based triglyceride similar to palm or coconut oil. This is an intermediate product that can subsequently be used to produce biodiesel. Their process uses a combination of enzymes to break down the cellulosic material. The program goal is to produce at least 30 gallons of fuel from every 2,000 pounds of waste material. About 80% of the world’s almonds are grown in the San Joaquin Valley, so the almond husks represent a California resource that would otherwise be landfilled or burned. While they’ll be working with grape and almond waste materials in this program, almost any cellulosic material can eventually be converted, such as paper, cardboard, tree cuttings, switch grass or sugar cane waste, he says. Menon & Associates is also working as a subcontractor on a DoD contract to produce jet fuel from cellulose and with the Navy on a process to create cellulosic-based fuel for troops that are deployed in the field.

The biotechnology company LS9 has employed synthetic biology and DNA-engineering technology to modify the genetic pathways of bacteria to make fatty acids, which can then be turned into fuel, from renewable feedstocks, such as sugar. This one step fermentation process uses DesignerMicrobes™ to efficiently convert renewable feedstocks to a portfolio of "drop in compatible" UltraClean™ fuels and sustainable chemicals (LS9 website, 2010). The bio-crude oil yielded by this DesignerMicrobes™ process contains no sulfur. LS9 planned to build a pilot plant to test the process, to produce improved biodiesel, and to provide synthetic biocrudes to refineries for further processing. Scientists at LS9 have demonstrated that engineered *E. coli* can convert sugars or hemicellulose into biodiesel (Steen et al., 2010).

Amyris Biotechnologies of Emeryville, CA has developed a fermentation process that uses genetically engineered yeasts to convert sugars into a class of compounds called isoprenoids (Peralta-Yahya and Keasling, 2010). These compounds include pharmaceuticals, nutraceuticals, flavors and fragrances, industrial chemicals and chemical intermediates, and fuels. The Amyris process focuses on a hydrocarbon called farnesene. This hydrocarbon forms a separate phase that floats at the top of the fermentation broth, and is processed into a renewable diesel in the finishing process. The production process can utilize a wide range of feedstocks, but Amyris is initially focusing on sugarcane, as a low-cost feedstock. Amyris opened a 10,000 gallon per year demonstration plant in Campinas Brazil in 2009. Amyris Brasil S.A., a subsidiary of Amyris, Inc., is running a demonstration test with the Sao Paulo bus fleet during the last 6 months of 2010.

5.2.2.7 Process Requirements and Considerations

A detailed study conducted by the NREL examined the processing requirements of a biochemical ethanol process. This study assumed that 2,200 dry tons per day of biomass feedstock (composed of corn stalks, leaves, cobs, and husks) would be pre-treated with dilute sulfuric acid at a high temperature to release hemicellulose and other compounds. In addition, lime would be added to remove compounds that are toxic to the fermenting organisms. The study also assumed that lignin and unconverted cellulose are combusted in a circulating fluidized bed boiler to generate process steam and electricity. Utilizing the non-fermentable biomass for energy reduces the consumption of natural gas or other fossil fuels (Aden et al., 2002).

The biochemical facility modeled by NREL would process 2,200 dry tons per day of biomass to produce roughly 200,000 gallons of ethanol per day. Relevant performance parameters of the biochemical ethanol process are provided in Table 5-2.

Table 5-2: Performance Characteristics for a Biochemical Ethanol Facility.

Parameter	Value
Biomass consumption (dry ton/day)	2,200
Natural gas consumption (MW, LHV)	0
Ethanol yield (gallons/dry ton of biomass) *	90
Ethanol production (million gallons/year) * **	69

Source: Aden et al., 2002. Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL/TP-510-32438.

Notes: * The NREL study modeled a process that would employ dilute acid prehydrolysis and enzymatic hydrolysis.

** Assumes 8,406 hours of operation per year.

Water requirements are another important consideration for biochemical processes. For current biochemical processes, water requirements are slightly higher than the water requirements of conventional ethanol facilities. The total consumption is estimated to be approximately 6 gallons of water per gallon of ethanol produced. For comparison, the water requirements for conventional ethanol processes are typically in the range of 2 to 4 gallons of water per gallon of ethanol produced.

Enzymatic hydrolysis uses several consumables throughout the process. Most notably, cellulase enzymes break down complex cellulose polymers into simple sugars that are easily fermentable. Other chemicals are used for pretreatment of the biomass, nutrients for microorganism growth, pH control, scale removal, oxygen removal, and treatment of water streams (including boiler feedwater, cooling water and wastewater).

5.2.3 *Biochemical-Based Cellulosic Infrastructure, Distribution, and Utilization*

The distribution and utilization of ethanol from cellulosic biochemical processes would be similar to that for alcohols produced from more conventional means, as discussed in chapters 3.2 and 3.3.

5.3 Technical Limitations for Biochemical-Based Cellulosic Processes

5.3.1 *Biochemical-Based Cellulosic Feedstock Limitations*

Feedstock development is another area for potential research funding. High yields and faster growing feedstocks are among the most important goals, allowing higher productivity for a given land area. Other important considerations, or areas where improvements could be made, include drought resistance, reduced fertilizer demands, recalcitrance, and greater carbohydrate content. Fundamental research of the characteristics of different feedstocks, and engineering plant cell walls in poplar and switchgrass to be less recalcitrant, could also be important. Much of the research in feedstock development has focused on “energy crops”, such as switchgrass, which could be grown exclusively for fuel production. Feedstocks applicable for California would primarily be those that could be grown under the semi-arid and other climates found in

California, with agave being a good example of a fast growing, draught tolerant plant (Austin, 2010).

5.3.1.1 Biochemical-Based Cellulosic Feedstock Economic Considerations

The costs to grow and harvest energy crops and the associated selling price of these feedstock crops will be an important factor in the selection of different feedstocks. There are many factors that must be considered when estimating or measuring cellulosic feedstock cost. If the feedstock is planted specifically for conversion to fuel, then all the costs to prepare the soil, plant the seed, grow the crop, harvest the crop, and transport it to the processing site have to be determined. If the feedstock grows naturally, without help from mankind, then the cost to harvest and transport it to the processing facility must be determined. If the feedstock is a waste product, then the cost to collect it and transport it to the processing facility must be determined.

Coughlin and Fridley (2008) calculated the switchgrass price farmers would receive for various scenarios assuming the produced ethanol had to be competitive with corn ethanol. There estimates are shown in Table 5-3. In 2008, farmers were selling field crops at a median price of \$750/ha. Therefore, there would be no incentive for farmers to grow switchgrass on traditional cropland, with the exception of the most optimistic situation, high yield, high efficiency.

Table 5-3: Implied Value in \$/ha that a farmer would earn selling switchgrass feedstock

<i>Switch grass yield t/ha</i>	<i>Average Efficiency (\$/ha)</i>	<i>High Efficiency (\$/ha)</i>
7	322	459
9	414	590
11	506	721
13.5	621	885

Coughlin and Fridley (2008) also looked at logistical considerations, including irrigation and location of refineries. They assumed that irrigated land used for the production of high-value food crops would not be converted to switchgrass production. Their analysis indicates there are approximately 2.7 million acres of pasture, hay production, and native vegetation land, primarily in the Central Valley, which could be irrigated to grow switchgrass. The authors estimated the economics based upon switchgrass yields from 7 to 13.5 tons/hectare (t/ha). The analysis considered how many refineries would be needed to keep the average switchgrass transportation distance to the refinery economically viable. The minimum number of refineries is 9 and the maximum is 19, with average transportation distances from 32 to 89 miles. The amount of switchgrass too distant from a refinery for economic transportation ranged from 21.5 to 14.1% of the total switchgrass grown. It is not at all certain that the water requirements can be met. Even if the water requirements could be met, and all irrigated pasture and fibercrop land were diverted to switchgrass production, the total output of ethanol would only supply 1.2 – 4.1% of California’s gasoline requirement, which is less than the current blending mandate.

The cost of nitrogen will be a substantial component of the non-harvest cost of managing and maintaining land dedicated to perennial grass energy crops. Haque et al. (2008) conducted experiments to determine the cost to produce four different perennial grasses as a function of the nitrogen fertilizer rate and using one or two harvests per year. The study utilized a split-plot

arrangement with four 131 feet by 180 feet plots, and nitrogen fertilizer rates of 30, 60, 120, and 240 lbs. per acre. The authors considered all of the costs for preparing plots, planting the grasses (establishment costs), and the annual maintenance and harvesting costs. The perennial grasses for the study were switchgrass, burmudagrass, weeping lovegrass, and flaccidgrass. Fertilizer costs ranged from \$36 to \$59 per ton of biomass produced. For this study, switchgrass fertilized at 60 lbs nitrogen/acre and harvested once a year was the least-cost strategy, with the other grasses being 20 to 26% higher.

Several studies have looked at the economics of energy crops in different states. Lazarus (2008) calculated the breakeven prices for various cellulosic stocks that could be grown in Minnesota and corn stover. The breakeven prices are the per-ton price needed to bid land away from current land uses, which are corn grain, soybeans, wheat, and hay, to grow energy crops. . The yields varied with crop and the number of years the crop was grown. The minimum yield was 1 ton/acre and the maximum 4 tons/acre. The breakeven prices are shown in Table 5-6. Busby et al. (2007) calculated yield and production costs for three potential dedicated grass energy crops in Mississippi and Oklahoma. They report establishment year cost and maintenance and harvest year cost in dollars per acre for a single and a double harvest. Their cost estimates are shown in Table 5-7. Busby et al. (2007) found that in Mississippi, based upon actual cost, switchgrass with a double harvest method was the cheapest feedstock, while in Oklahoma switchgrass with a single harvest method was the cheapest. Because growing conditions, the growing season, crops being grown, labor costs, etc. are very different from California; an equivalent analysis specific to California is being performed by the CEC in conjunction with the California Department of Food and Agriculture.

Table 5-4: Breakeven price for various biomass products in Minnesota

	<i>Corn Grain Stover Collection</i>	<i>Corn No Grain with Stover Collection</i>	<i>Soybeans</i>	<i>Wheat</i>	<i>Corn Stover Added Cost</i>	<i>Grassland high fertilization</i>	<i>Grassland low fertilization</i>	<i>Hybrid poplar</i>	<i>Willow</i>
Corn stover breakeven price/ton					\$ 50				
Grassland, high fertilization breakeven price/ton	\$ 150	\$ 157	\$ 124	\$ 90		\$ 77			
Grassland low fertilization breakeven price/ton	\$ 247	\$ 262	\$ 198	\$ 135			\$ 110		
Hybrid poplar breakeven price/ton	\$ 143	\$ 150	\$ 121	\$ 92				\$ 81	
Willow breakeven price/ton	\$ 128	\$ 134	\$ 108	\$ 81					\$ 72

The stover breakeven price was calculated as the difference between a corn grain budget without stover removal and the additional machinery, labor costs, and fertilizer nutrient replacement required to collect the corn stover for energy use.

Table 5-5: Cost of Producing Potential Biomass Feedstocks in Mississippi (SH = Single Harvest, DH = Double Harvest)

		<i>Switchgrass</i>		<i>Giant Miscanthus</i>		<i>Eastern Gammagrass</i>	
		SH	DH	SH	DH	SH	DH
Mississippi							
Establishment Cost per acre		286.29	286.29	803.20	803.20	318.87	318.87
Maintenance and Harvest Cost per acre		271.20	301.77	253.02	283.59	267.52	297.78
Oklahoma							
Establishment Cost per acre		123.35	123.35	834.63	834.63	140.15	140.15
Maintenance and Harvest Cost per acre		81.02	118.41	71.59	102.69	63.77	89.70
Mississippi							
Cost per ton (Est. Amortized 5 years)	Actual	32.18	28.66	36.30	33.45	139.72	42.54
	Predicted	27.51	26.25	33.74	32.53	71.10	44.06
Cost per ton (Est. Amortized 15 years)	Actual	28.50	25.66	27.35	25.74	122.14	37.62
	Predicted	24.39	23.48	25.42	25.04	62.23	38.85
Oklahoma							
Cost per ton (Est. Amortized 5 years)	Actual	15.96	22.07	48.90	51.45	23.33	31.18
	Predicted	15.97	20.87	48.44	50.17	26.28	29.82
Cost per ton (Est. Amortized 15 years)	Actual	13.54	19.57	28.11	31.88	21.12	26.36
	Predicted	13.61	18.46	28.26	30.74	18.64	25.31

The actual costs based upon the mean yields harvested from the test plots. Predicted costs are based on the estimated yield expected to be reached by each species. The establishment year cost and maintenance cost is the same for the single and double harvest because it is only paid in the year the seed is planted.

5.3.2 Biochemical-Based Cellulosic Production Limitations

The most important barriers to the expansion of cellulosic biochemical ethanol for transportation applications are the production costs.

Pretreatment is the most expensive operation within the production process, followed by enzymatic hydrolysis of the pretreated cellulose and the costs of making enzymes to carry out this process. The pretreatment process has an impact on all subsequent processes that utilize the products of pretreatment, and the pretreatment degradation products can have inhibitory effects on the subsequent hydrolysis and fermentation processes. A number of processes can be used to open up the plant structure to make cellulose, and other polymeric carbohydrates left in the solids, accessible to enzymes, including acid hydrolysis, steam explosion, ammonia fiber expansion, organosolv, sulfite, sulfur dioxide, alkaline wet oxidation, and ozone pretreatments. Dilute sulfuric acid, sulfur dioxide, ammonia, neutral pH, and lime have been used to achieve high sugar yields from corn stover. These pretreatments are not universally successful with all types of biomass, however. Continued advances are needed in pretreatment technologies to improve sugar yields, reduce the chemical and energy requirements of the process, and minimize

the production of inhibitory byproducts. A better understanding of the factors that promote recalcitrance in the biomass feedstocks is also needed to identify critical pathways in improving process cost effectiveness.

Cellulase enzymes remain one of the most significant cost contributors to processing cellulosic biomass. Enzymes with greater specific activity are needed to increase reaction rates and achieve high conversions with much less enzyme. Currently, approximately a quarter pound of enzymes is required to produce a gallon of ethanol with high yields. Enzyme mixtures that can effectively release the hemicelluloses left in pretreated solids are also important for achieving the high yields needed for large-scale competitiveness. Although some progress has been made by industrial enzyme producers, cost-effective enzyme production technologies are still not available. Several of the leading developers of biochemical ethanol processes are developing proprietary enzymes. For example, as noted above, Mascoma claims to have developed a micro-organism capable of producing both enzymes and ethanol. In addition to efficient hydrolysis of cellulosic feedstocks, these enzymes must demonstrate this ability in the presence of product inhibitors. Some major enzyme companies have also recently announced significant cost reductions.

Another important area is optimizing the process integration between the different processing steps. Enzyme production, hydrolysis, and fermentation, each involve their own set of complex reactions, which make it difficult to reduce or consolidate the number of processing steps. Breakthroughs in one area of production must be integrated with other areas of the production process and then optimized. While this represents an important limitation on production efficiency, there is still limited practical experience in process integration for biochemical processing.

Some technoeconomic analyses have been conducted to provide a more quantitative measure of the production costs for cellulosic ethanol and the various steps in the process. Over the last two decades, the DOE/NREL has conducted a series of technoeconomic analyses on biochemical cellulosic ethanol, with the most recent one published in 2009 (Aden and Foust, 2009). These production cost estimates are largely based on the technoeconomic analysis of currently available technologies, since there are currently no commercial scale cellulosic ethanol plants in operation. Figure 5-2 depicts the conceptual process design on which DOE/NREL analysis is based. In this design, corn stover is chosen as a model feedstock and dilute acid is used as pretreatment technology. After pretreatment, the hydrolysate is subjected to solid/liquid separation and conditioning steps to neutralize the acid and remove inhibitors. Simultaneous saccharification and fermentation (SSF) is then carried out with the combination of enzymes and fermentative microorganisms followed by a final distillation and dewatering step to produce fuel ethanol. The solid residues after SSF are burned to generate steam and electricity.

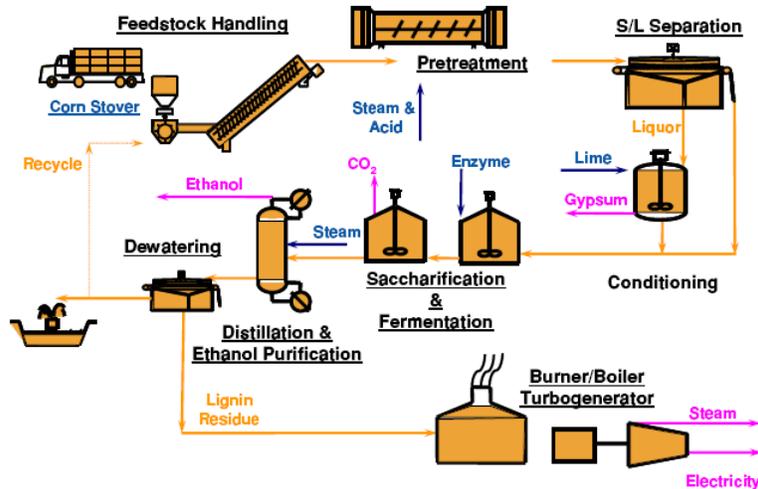


Figure 5-2: Overall conceptual process design of DOE/NREL mode

Based on a plant size of 2,000 dry metric tons per day of corn stover, the conversion cost for the previous described process design was analyzed and the minimum ethanol selling price (MESP) was further broken down into costs for each process area. As illustrated in Figure 5-3, the single largest cost to the process is the feedstock cost (including handling) at 38% or \$0.51/gallon ethanol. The boiler/turbogenerator also presents a significant portion of the overall capital cost, though some of this cost can be offset by the credits from excess steam and electricity. The next largest cost area is pretreatment at 19% or \$0.25/gallon ethanol. The cost of enzyme assumed in this analysis is roughly \$0.10/gallon ethanol, which is relatively low. The authors made a special note that their analysis was only a snapshot of what cost estimates may be. It's very difficult to assess costs with certainty since commercial-scale cellulosic biorefineries are not yet operational and process yields are not proven but simply estimated. A sensitivity analysis helps determine which process parameters have the most impact on the overall economics. It is shown that the largest impact factors include plant size, feedstock cost, composition of feedstock, and the cellulase enzyme cost.

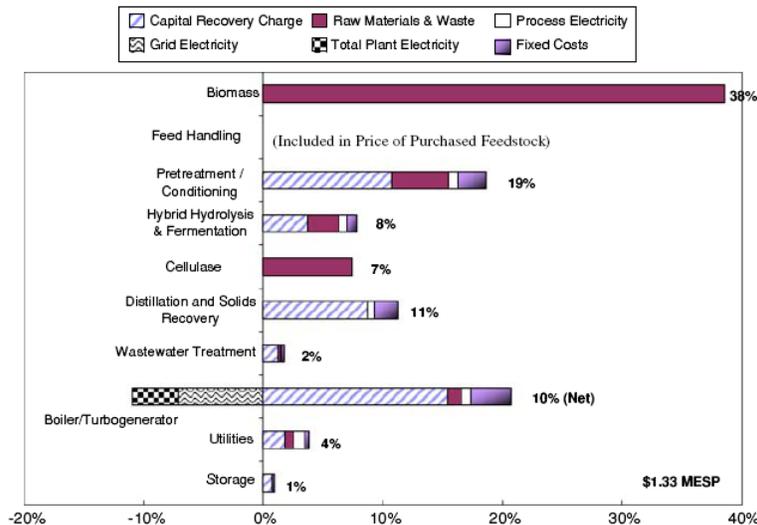


Figure 5-3: Cost contribution of each process area to the overall MESP

At a December 2005 DOE workshop (DOE, 2006a), it was concluded that it would take ~15 years for cellulosic ethanol to become cost competitive. As shown in Figure 5-4 from this report the development is expected to proceed in three phases. The first phase would involve research on plant genomics (genes, principles, controlling factors for cell walls), cell walls (enzyme interactions, deconstruction to sugars, recalcitrance factors), multisugar fermentation (tolerance, control), and systems biology for biomass to biofuels. While this would be the primary focus for the first 5 years (~2006–2010) the research would continue indefinitely. During the second 5 year stage (~2011–2015), based upon results from the research, the technology deployment would take place. Technology deployment will include: plant biomass optimization (sustainability, yield), enzyme improvement (range, tolerance, consolidation), high-temperature multisugar fermentors (Simultaneous Saccharification and Cofermentation (SSCF), Consolidated Bioprocessing (CBP)), process tolerance, and Bioenergy systems engineering for various regions. The final phase (~2016–2020) will be Bioenergy systems integration: sustainable agriculture, consolidated processing, and fusion of the economic value chain (agriculture, energy, biotech).

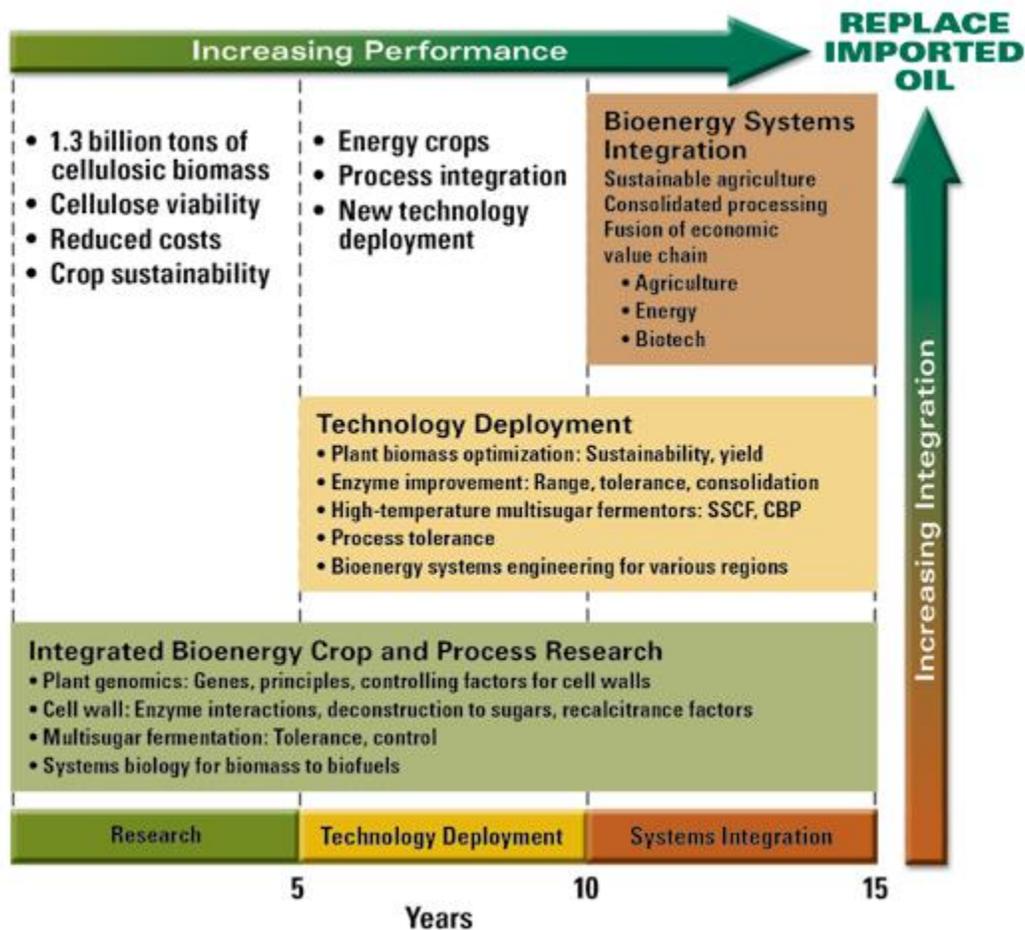


Figure 5-4: Phased Development of Bioenergy Systems

Since 2005, there is no subsequent report that gives an update on the current development status against the projected phases development timeline. Good technical improvements have been

made over the past five years, especially with the synergistic efforts of the three DOE funded bioenergy research centers. Reflecting these developments, a recent technical note published by DOE/NREL examined the status for the year 2008 and established a 2008 State of Technology (SOT) model (Humbird and Aden, 2009). Based on this update, several key biochemical platform accomplishments were achieved in the areas of feedstock development, pretreatment, conditioning, enzymatic hydrolysis, and fermentation. The new development of new feedstocks has enabled the addition of energy crops to the platform. A new ammonium hydroxide conditioning configuration has been developed and shown to effectively reduce sugar loss and inhibition to fermentation and eliminate the need to dispose of gypsum. Based on those technical updates, the SOT MESP for FY 2008 was \$2.61, slightly down compared with FY 2007 at \$2.61/gal. MESP's beyond 2008 were also forecast based on research targets. It is expected that by 2012, the MESP can be reduced to \$1.49, thus meeting the ethanol cost goals put forth by DOE in terms of MESP obtaining a 10% internal rate of return. These cost projections are shown in Figure 5-5. This SOT also pointed to research directions and critical process improvements to further reduce the costs in areas such as pretreatment, enzymatic hydrolysis, fermentation and delivered feedstock price.

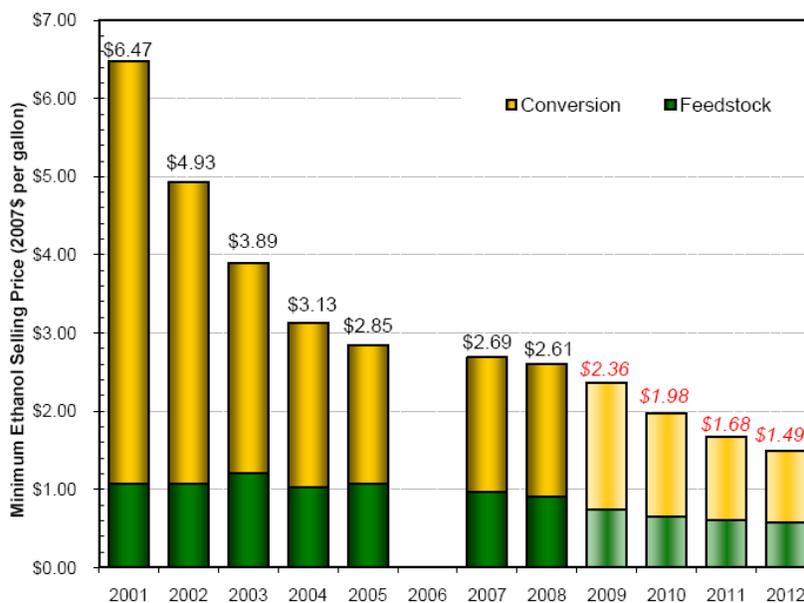


Figure 5-5: DOE/NREL Projection toward 2012

5.3.3 Biochemical-Based Cellulosic Infrastructure and Utilization Limitations

The distribution and utilization of ethanol from cellulosic biochemical processes would face the same problems and solutions discussed for conventional alcohols in sections 3.2 and 3.3.

5.4 Environmental and Other Considerations

CARB (2009a) evaluated the Well to Wheel (WTW) GHG emissions for cellulosic ethanol produced from farmed trees and forest waste using the CA-GREET. These results are provided in Table 5-9. The estimates for the carbon intensity value for cellulosic ethanol produced from both farmed trees and forest trees were similar and around 20 gCO₂e/MJ (CARB, 2009b,c).

These values are well below the corresponding carbon intensity value for gasoline. A preliminary land use change analysis was performed for non-food crop based cellulosic feedstocks. The land use change values were estimated to be 18 gCO₂e/MJ for cellulosic feedstock grown on marginal land. For the forest trees, the contribution for forest waste collection and transportation were 8.61 and 3.67 gCO₂e/MJ, respectively. Other estimates of the lifecycle GHG emissions benefits from cellulosic ethanol have also shown significant reductions relative to gasoline, although not quite as significant as those from CARB’s evaluations. Delucchi (2006) estimated a 44% reduction in total fuel cycle CO₂-equivalent emissions for cellulosic ethanol (E90) made from switch grass compared to conventional gasoline. Aden (2009) more recently estimated greenhouse gas emission reductions of 40-50% for cellulosic ethanol production from feedstocks such as corn stover, switchgrass, and wheat straw. Other environmental issues with the use of ethanol in vehicles, such as evaporative emissions, would have essentially the same impacts as discussed previously in chapter 3.4.

Table 5-6: Adjusted Carbon Intensity Values for Gasoline and Cellulosic Ethanol.

Fuel	Pathway Description	Carbon Intensity Values (gCO ₂ e/MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Gasoline	CARBOB – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	95.86	0	95.86
Cellulosic Ethanol	Cellulosic ethanol from farmed trees by fermentation	2.40	18	20.40
	Cellulosic ethanol from forest waste	22.20	0	22.20

5.5 On-going Research

5.5.1 *Feedstocks*

Feedstocks is one of the main areas of ongoing research for cellulosic biochemical production. There are a number of considerations that must be taken into account when developing improved feedstocks. High yields and faster growing feedstocks are among the most important goals, allowing higher productivity for a given land area. Biomass feedstocks must also be available on a very large scale to have meaningful impact. The US DOE production goal is to provide 130 million dry tons/year (MDT/yr) by 2012 and 250 MDT/yr by 2017 of high quality feedstock. Other important considerations or areas where improvements could be made include drought resistance, reduced fertilizer demands, recalcitrance, and greater carbohydrate content.

Much of the research in feedstock development has focused on “energy crops”, which are grown exclusively for fuel production. For energy crops, switchgrass is one of the preferred species because it is a native “well-behaved” perennial grass which develops a deep, vigorous root system to acquire nutrients and water under diverse soil and climate conditions. Other grasses which have received consideration as energy crops for ethanol production are: Big Bluestem Genotype, Forage Sorghum, Sericea Lespedeza Serala, Sweet Sorghum, Tall Fescue (AFAVDC, 2009), Giant Miscanthus, Eastern Gammagrass (Busby et al., 2007) and burmudagrass, weeping lovegrass, and flaccidgrass (Haque et al., 2008).

For California, it is important to be evaluating feedstocks that could be grown under conditions found within the State. This would include feedstocks that could be grown under the semi-arid and other climates found in California. Agave is one very good example of a fast growing, drought tolerant plant that could be grown under these conditions in California that could be used for research directed towards in-state production.

There are some optimistic estimates about the potential for productivity increases into the future. One energy crop firm, Ceres, projects that average productivity of cellulosic energy crops of 15 tons per acre (roughly 3 times current productivity for switchgrass) can be achieved across a broad range of geographic and climate regions, including most of the continental US, in ten years given an aggressive effort using modern breeding technologies. Other estimates indicate that future increases in biomass production per unit land and fuel production per unit biomass could together result in a roughly tenfold increase in land fuel yield compared with today.

Research into cellulosic biomass feedstocks is an important part of DOE's overall research program. In addition to the development of feedstocks for optimal yield and growing conditions, DOE is also emphasizing fundamental research of the characteristics of the different feedstocks. Some of the main focuses of DOE funding in the area of feedstock development at the Federal level include engineering plant cell walls in poplar and switchgrass to be less recalcitrant. This would increase the total biomass produced per acre while decreasing the need for harsh chemical pretreatments. The DOE is also funding work to engineer model plants and energy crops to produce new forms of lignin and starches that can more readily be processed to fuels. Work is also being funded to enhance lignin degradation by modifying the cross links between lignin and other cell-wall components. This research includes the sequencing of DNA from bioenergy crops, identifying genes and pathways that improve biomass productivity, and fundamental studies of the cell wall structure of different biomass feedstocks.

The DOE is evaluating potential gains that can be obtained in reducing production costs, including the harvesting, handling, storage, and preprocessing of feedstocks (Rodgers, 2009). The DOE goal is to reduce these feedstock production processing costs to a level of \$0.39/gallon by 2012 and to \$0.33/gallon by 2017. Some challenges in this area include the low density and fibrous nature of cellulosic biomass; making it difficult and costly to handle. There is also a need to understand the environmental effects of feedstock production and residue collection on sustainable production. Understanding the physical, chemical, and other properties of feedstock in a real-time basis or the development of processor standards or specifications for feedstock may also facilitate feedstock processing. While these topics may be important for the overall development of cellulosic biomass production, we feel these issues are best funded on a larger scale at the Federal level rather than through PIER.

On June 2, 2010 the Golden Field Office of DOE released a Funding Opportunity Announcement (FOA) for "Development of Methodologies for Determining Preferred Landscape Designs for Sustainable Bioenergy Feedstock Production Systems at a Watershed Scale" (DOE, 2010b). While EISA (2007) and the Renewable Fuel Standard (RFS2, 2010) require the production of 36 billion gals per year of biofuels from domestically produced feedstocks by 2022, including 21 billion gallons per year of advanced biofuels from cellulosic

feedstocks, it is not known at this time if this is a sustainable possibility. It has been calculated that, to displace 30 percent or more of the country's present petroleum consumption, approximately one billion dry tons of sustainably produced feedstocks would need to be produced each year. It is anticipated that the feedstock required to achieve the anticipated rapid expansion of the commercial domestic biofuels industry will come predominantly from dedicated energy crops (Perlack, et al., 2005).

The intent of the FOA is to quantify and better understand the relative impacts on the environment of different strategies for producing large quantities of intensively managed high-yielding energy crops, and crop and forestry residues at the watershed scale. The nascent cellulosic biomass industry and its stakeholders require this information and knowledge for sustainable implementation of energy crop production systems at the watershed scale. For the purposes of this FOA, sustainability refers to the environmental, social, and economic considerations necessary to meet current bioenergy needs without inhibiting the ability to meet current and future needs for food, feed, fiber, water, bioenergy, biodiversity, etc. However, although sustainability encompasses these three elements, for purposes of this FOA they are most interested in filling gaps in the understanding of the interplay between environmental and economic considerations.

A study for the United Kingdom (Howes, et al., 2009) has also noted that there are many gaps to be researched to determine if biofuels can be sustainably produced and fulfill all the promises of being more environmental friendly.

5.5.2 Production

Pretreatment is one of the most important aspects of the production process, and a critical step in reducing the overall production costs. Pretreatment studies are being conducted both to improve the pretreatment process and to study how various feedstocks react to different pretreatments and what the resulting products are. The pretreatment studies designed to evaluate feedstocks are usually done with the more traditional processes, including continuous steam explosion or dilute acid pretreatment. In these studies, the parameters of the pretreatment process such as temperature, pressure, and acid concentration can be optimized for different feedstocks. Other processes are in more of a development stage, including Ammonia Fiber Explosion (AFEX), Ammonia Recycle Percolation (ARP), and lime pretreatment. Ammonia Fiber Explosion involves mixing water, ammonia, and biomass into a reactor at high pressure (200 – 700 psi) for varying temperatures (60 – 200 °C), and then suddenly reducing to atmospheric. Ammonia Recycle Percolation involves flowing the biomass and ammonia through a flow-through column reactor. Cellulose can also be treated and broken down with lime and pure oxygen at high temperatures (100 – 200 °C) and high pressure.

5.5.3 DOE Bioenergy Research Centers

To facilitate meeting the EISA goals for renewable fuel development, the USDOE established three Bioenergy Research Centers (BRCs) in September 2007 with each center receiving \$125MM in funds to assemble a multidisciplinary team from universities, national laboratories, nonprofit organizations, and a range of private companies. The three centers are:

- DOE BioEnergy Science Center (BESC) led by DOE's Oak Ridge National Laboratory in Oak Ridge, Tennessee.
- DOE Great Lakes Bioenergy Research Center (GLBRC) led by the University of Wisconsin in Madison, Wisconsin, in close collaboration with Michigan State University in East Lansing, Michigan.
- DOE Joint BioEnergy Institute (JBEI) led by DOE's Lawrence Berkeley National Laboratory.

The three Centers are located in geographically distinct areas (Figure 5-6). One merit of the setting of DOE Bioenergy Research Centers is that it provides diverse and complementary scientific expertise. The research synergies are on a scale far greater than any effort in the past.

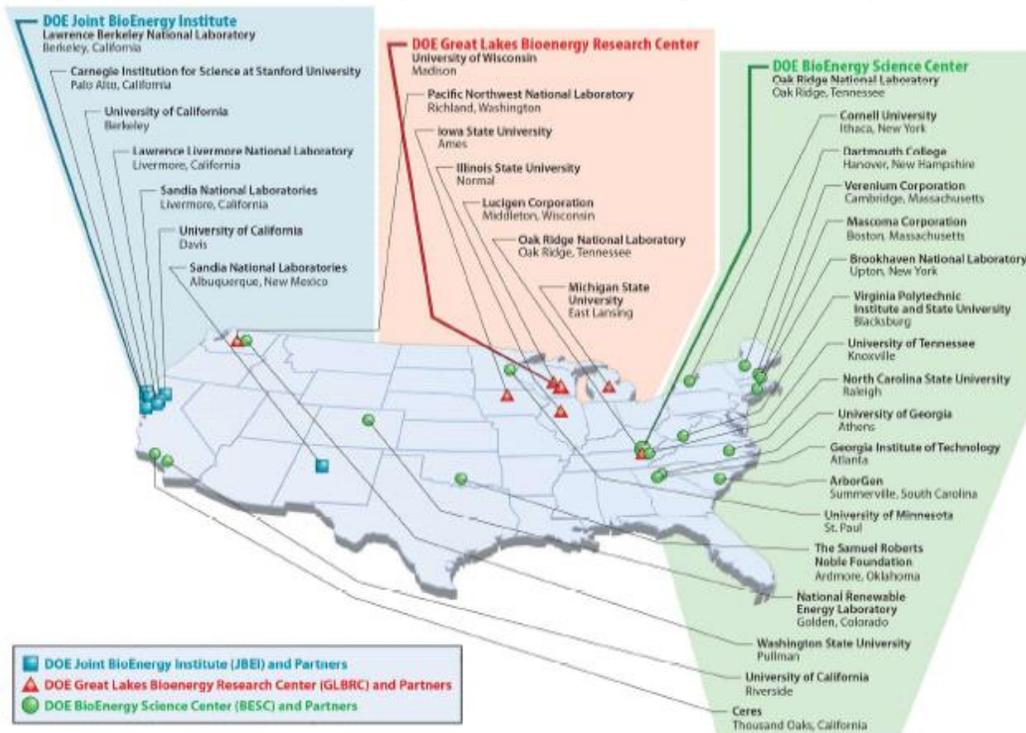


Figure 5-6. Bioenergy Research Centers (BRCs) and their constituents

Each of the research centers is utilizing a different strategy to address the different key research areas. A summary of the approaches for each of the centers main research areas is provided in Table 5-7.

Table 5-7. DOE Bioenergy Research Center Strategies at a Glance*

Grand Challenge: Development of Next-Generation Bioenergy Crops

- Center Strategies**
- **GLBRC** – Engineer “model” plants and potential energy crops to produce new forms of lignin and more starches and oils, which are more easily processed into fuels.
 - **JBEI** – Enhance lignin degradation in “model” plants by changing cross-links among lignin subunits; improve deconstruction and subsequent fermentation by altering linkages between lignin and other cell-wall components; translate genetic developments to switchgrass.
 - **BESC** – Decrease or eliminate harsh chemical pretreatments by engineering plant cell walls in poplar and switchgrass to be less recalcitrant; simultaneously increase total biomass produced per acre.

Grand Challenge: Discovery and Design of Enzymes and Microbes with Novel Biomass-Degrading Capabilities

- Center Strategies**
- **GLBRC** – Identify combinations of enzymes and pretreatment needed to digest specific biomass types; express biomass-degrading enzymes in the stems and leaves of corn and other plants.
 - **JBEI** – Develop new ionic liquid pretreatments that can completely solubilize and fractionate biomass components; improve performance and stability of enzymes obtained from the rainforest floor and other environments; engineer, through directed evolution, highly efficient cellulase enzymes.
 - **BESC** – Screen natural thermal springs to identify enzymes and microbes that effectively break down and convert biomass at high temperatures; understand and engineer cellulosomes (multifunctional enzyme complexes for degrading cellulose).

Grand Challenge: Development of Transformational Microbe-Mediated Strategies for Biofuel Production

- Center Strategies**
- **GLBRC** – Start with an ethanol-producing microbe and add lignocellulose-degrading capabilities to substantially reduce costs.
 - **JBEI** – Connect diverse biological parts and pathways to create entirely new organisms that produce fuels other than ethanol; engineer organisms to produce and withstand high concentrations of biofuels; derive useful chemical products from lignin degradation.
 - **BESC** – Start with a lignocellulose-degrading microbe and add ethanol-producing capabilities to substantially reduce costs; develop a knowledgebase and pathway analysis tools to aid this manipulation.

*BESC: BioEnergy Science Center; GLBRC: Great Lakes Bioenergy Research Center; JBEI: Joint BioEnergy Institute. (Adapted from: <http://genomicscience.energy.gov/centers/>)

Some of the highlights of the research at each of the centers are provided below.

Bioenergy Center Research Highlights

1. BESC

- High-throughput biomass characterization pipeline
- Advances in microbe-mediated consolidated bioprocessing (CBP)
- New insights from computer simulations build a foundation for cellulosome design
- Development of a novel in vitro assay for xylan biosynthesis
- New cellulose-degrading enzymes discovered by screening environmental DNA

2. JBEI

- Development of ionic liquid (IL) pretreatment
- Re-engineering microbes to produce novel biofuels
- New strategy for faster microbial metabolic studies
- Analysis of plant gene family that inhibits deconstruction
- Phylochip for rapidly screening thousands of microbial species
- Structural characterization of a heat- and acid-tolerant enzyme

3. GLBRC

- Using 2D NMR to understand plant cell-wall composition and function
- Enzymes for biomass pretreated with AFEX
- Two-step chemical method for converting untreated biomass to biofuel
- Sustainable biofuel landscapes

5.6 Recommendations for Biochemical Cellulosic Fuels Research

Biochemical cellulosic ethanol processes may represent the most likely pathway for near-term commercialization of second generation biofuel production in the United States. Legislative requirements provide a target of at least 16 billion gallons of cellulosic ethanol to be produced by 2022 (EISA, 2007). There has been a significant increase in the research funding being allocated to cellulosic biomass applications. This includes, at the Federal level, the funding of the three BRCs for \$125 million each over 5 years. There are also a significant number of private companies developing and optimizing the enzymes and microorganisms necessary for biochemical production of ethanol from cellulosic feedstocks, and the U.S. DOE has provided substantial financial assistance to companies that are developing commercial-scale facilities. Given this level of interest in biochemical cellulosic ethanol processes, it is likely that this will be a rich-area of research progress in biofuel production over the next few years and one worthy of PIER funding support, especially for programs that can be targeted for greatest use within the State. Some of the more important areas for research funding are discussed below.

Excluding biomass feedstock supply chain issues, the most significant technical barrier to the commercialization of cellulosic ethanol is the lack of efficient and economical cellulose pretreatment and enzymatic hydrolysis processes. The production process involves a number of steps including pretreatment, enzymatic hydrolysis, fermentation, and product recovery. Pretreatment is the most expensive operation within the production process, followed by enzymatic hydrolysis of the pretreated cellulose and the costs of making enzymes to carry out this process. The pretreatment process also has an impact on all subsequent processes that must utilize the products of pretreatment. Any degradation products from pretreatment can have inhibitory effects on subsequent hydrolysis and fermentation processes. The choice of pretreatment is also closely related to the choice of feedstock and vice versa.

One of the main difficulties in processing cellulosic biomass is the natural resistance or recalcitrance that locks in sugars in the lignocellulosic biomass feedstocks so they are not available for microbial breakdown. A variety of methods can be used in the pretreatment process. Size reduction is often an important first step preparing the biomass feedstock for subsequent chemical processing. A number of processes can then be used to open up the plant structure to

make cellulose and other polymeric carbohydrates left in the solids accessible to enzymes including acid hydrolysis, steam explosion, ammonia fiber expansion, organosolv, sulfite, sulfur dioxide, alkaline wet oxidation, and ozone pretreatments. Dilute sulfuric acid, sulfur dioxide, ammonia, neutral pH, and lime have been used to achieve high sugar yields from corn stover. These pretreatments are not universally successful with all types of biomass, however.

There are many aspects of pretreatment that can be addressed through continuing research. Continued advances are needed in pretreatment technologies to improve sugar yields, reduce the chemical and energy requirements of the process, and minimize the production of inhibitory byproducts. There is still a lack of understanding of the factors that promote recalcitrance in the biomass feedstocks. This lack of understanding makes it more difficult to identify critical pathways in improving process cost effectiveness. The roles that lignin and other biomass components play in impeding access to cellulose are also not well understood nor are the properties that determine the susceptibility of cellulosic substrates to hydrolysis.

Cellulase enzymes remain one of the most significant cost contributors to processing cellulosic biomass. Enzymes with greater specific activity are needed to increase reaction rates and achieve high conversions of both the C5 and C6 sugars with much less enzyme. Currently, approximately a quarter pound of enzymes is required to produce a gallon of ethanol with high yields. Enzyme mixtures that can effectively release the hemicelluloses left in pretreated solids are also important for achieving the high yields needed for large-scale competitiveness. Although some progress has been made by industrial enzyme producers, cost-effective enzyme production technologies are still not available. Several of the leading developers of biochemical ethanol processes are developing proprietary enzymes. For example, Mascoma (2009) claims to have developed a micro-organism capable of producing both enzymes and ethanol. In addition to efficient hydrolysis of cellulosic feedstocks, these enzymes must demonstrate this ability in the presence of product inhibitors. Some major enzyme companies also recently announced significant cost reductions.

Process integration is another key step that could provide important cost reductions. Process integration work is important to characterize the complex chemical interactions that exist between different processing steps. Consolidated Bioprocessing can be used to incorporate enzyme production, hydrolysis, and fermentation into a single process step. Lynd et al. (2008) found that this could be the most important development in cost reduction for cellulosic ethanol. Consolidated Bioprocessing uses the same microbes to anaerobically produce cellulase enzymes and ferment all of the released sugars into ethanol in the same vessel. The development of high-yield fermentative thermophiles that are matched to optimal cellulase operating conditions would be an important step toward this goal. More extensive process integration research can be utilized to generate integrated performance data and develop predictive mathematical models that can guide process optimization and scale-up. While this represents an important area of research, there is still limited practical experience in process integration. Additionally, research in process integration can require large or multidisciplinary teams and correspondingly larger program budgets.

Many of the areas of research interest for the growing of cellulosic feedstocks and cellulosic ethanol production are being funded already at the Federal level. The DOE's performance goals

for biochemical production are to reduce the estimated mature technology processing costs for converting cellulosic feedstocks to ethanol to \$0.92 per gallon in 2012 and \$0.60 per gallon in 2017. It is important that any efforts funded by PIER do not duplicate ongoing Federal efforts. One strategy would be to again focus on the unique processing requirements for feedstocks that would be specific to California, such as crops that are fast growing and drought resistant. PIER has an ongoing program with the California Department of Food and Agriculture to identify and evaluate food crops that can help identify California-based feedstocks suitable for further research. This research might be most effectively placed in developing and understanding the pretreatment of these feedstocks and the resulting degradation products. This could include fundamental studies of the cell walls of these materials or of the product materials. Subsequent to that, would be understanding the unique enzymatic requirements for the hydrolysis of these pretreatment products. It would also be very important to optimize the integrated process of pretreatment, enzyme production, enzymatic hydrolysis, and fermentation for these feedstocks as they are very interdependent and most research funded federally has failed to consider these interactions in process development.

Developing a better understanding of the overall sustainability and environmental impacts of energy crop production is another important area of research. This will be the focus of the DOE's Development of Methodologies for Determining Preferred Landscape Designs for Sustainable Bioenergy Feedstock Production Systems at a Watershed Scale" program discussed above (DOE, 2010b). Currently, there is only limited information and few tools for implementing and managing sustainable high-yield energy crops across the landscape. There is also little scientific information and no validated methodology for optimizing sustainable cellulosic biomass production systems beyond the plot and field scale to the watershed and larger scale. It is recommended that the PIER follow the progress of this DOE study to determine if any opportunities for funding in this area would be appropriate.

In summary, it appears that cellulosic ethanol will play an important role in the expansion of alternative fuels over the next 10 years and can utilize a broad range of feedstocks. As such, this is an area that PIER should allocate research funds to. Reducing production costs and developing improved feedstocks should be the highest priorities for research. As this technology is being funded extensively at the Federal level and in the private sector, PIER funds should be targeted toward development of feedstocks that would be most applicable for California and how to optimize the production processes for these feedstocks.

6 Gasification Conversion of Biomass to Liquids

6.1 Introduction

Thermochemical techniques can also be used for the conversion of biomass to various liquid fuels. Gasification is a thermochemical production technique that can be used to produce a range of different fuels for transportation. In the gasification process, high temperatures, with a controlled amount of oxygen, hydrogen, steam, and/or steam/hydrogen (termed partial oxidation, hydrogasification, steam gasification, and steam hydrogasification (Norbeck et al., 2008), respectively, are used to convert carbonaceous materials to a synthesis gas. The synthesis gas can then be converted into liquid products, typically via reactions over a catalyst. The feedstocks that can be used for gasification are wider than most of the other production techniques available. This includes natural gas, a wide variety of biomass, coal or other petroleum products. In this chapter, the technical development and ongoing research for gasification processes to liquid fuel for transportation fuels are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for gasification are provided. Pyrolysis and hydrogenation, other thermochemical processes, will be discussed in the next two chapters, respectively.

6.2 Development of Gasification Processes for the Production of Liquid Fuels

6.2.1 *Feedstocks for Gasification Processes*

Most carbon containing materials can be gasified to produce syngas. This is an important advantage for thermochemical processes, as they can utilize the widest range of feedstocks. The full range of feedstocks discussed in chapter 2 are generally applicable to gasification processes, including raw biomass, and processed biomass, such as pyrolysis oils, as well as coal and petroleum coke.

The breadth of feedstocks that can be utilized by thermochemical processes can be illustrated in part by evaluating the potential feedstocks in MSW. Hackett et al. (2004) noted that thermochemical processes can potentially convert all the organic portion of the MSW stream to useful products (where organic is defined as “containing carbon and hydrogen”), while biochemical processes can only convert the biodegradable fraction. They report that in MSW ~70% of the energy is from all the organics, while the biodegradable fraction contains <20% of the energy. In California, ~68% by wt of MSW is biomass related, ~11% by wt is non-biomass organic matter (non-film plastic ~5.0 wt%, film plastic ~3.9 wt%, and textiles ~2.1 wt %), and ~21% is inorganic (Hackett et al. 2004).

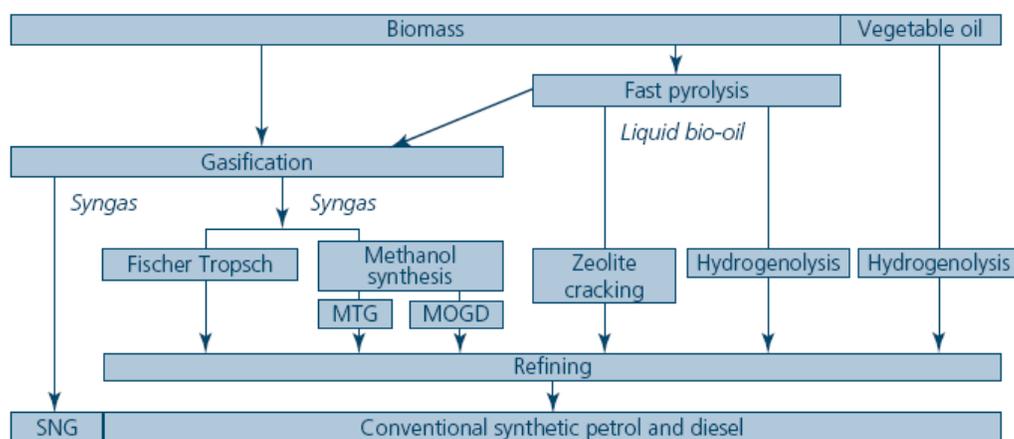
The consistency of the raw material will make a difference in the amount of pre-processing required and the gasification conditions. Liquids or gases, such as pyrolysis oils and natural gas, are easy to handle and inject into a gasifier, requiring little pre-processing, although pyrolysis oils must be contained in stainless steel equipment to prevent corrosion due to their high acid content. Fairly homogenous solids such as coal and coke require milling to a base consistency, but are readily adapted to gasification processes. Biomass is the most difficult material to gasify due to its inconsistent form, different moisture levels, and high level of impurities. The moisture

content in MSW, for example, varies from ~4 wt% to ~70 wt% for the biomass related portion and from ~0.2% to ~10 wt% for the non-biomass organic matter portion (Hackett et al. 2004). The ash/mineral matter in MSW varies from ~5.6 to ~16.1% by wt for the biomass related MSW and from ~2.1 to ~8.6% by wt for the non-biomass organic matter in MSW.

It is possible that there may be more constraints on the feedstocks that could be used for jet fuel production via thermochemical processes, or that the feedstock would need to be more homogeneous than would otherwise be needed for renewable diesel fuel production. For each possible source, the properties of the jet fuel produced will have to be determined, as it may not be possible to produce a jet fuel from some sources which will meet all the critical properties for safe flying.

6.2.2 Gasification Production for Liquid Fuels

Rather than separating the organic constituents of biomass and converting a portion of material to ethanol, thermochemical processes utilize gasification processes to convert the entirety of the biomass material into a syngas. Syngas is then converted to liquid products, typically via catalytic reactions. Instead of catalytic reactions to convert the syngas, some processes employ bacteria to ferment the hydrogen and carbon dioxide constituents of syngas into ethanol. Figure 6-1 illustrates a range of potential thermochemical pathways that can be used. This subsection will discuss separately gasification to produce a range of different end products, including Fischer-Tropsch diesel, methanol and methanol-to-gasoline, DME, and ethanol.



Source: “Sustainable Biofuels: Prospects and Challenges”, Royal Society, January 2008.

Figure 6-1: Conversion Routes for Producing Gasoline and Diesel Fuel from Biomass

6.2.2.1 Gasification Process Overview

Gasification can be separated into four stages. The first of these stages is a drying phase in which the moisture in the fuel evaporates. The second stage of gasification occurs as many of the tars and light gases trapped in the solid matrix of the fuel begin to exit the fuel. These light gases include H₂, CO, CO₂, H₂O, and CH₄. This stage is known as pyrolysis and can occur at temperatures from just above drying to almost 1,740° F. The extent of pyrolysis and the temperature range at which it occurs is dependent on the type of solid that is used as fuel in the

gasifier as well as the particle size of the fuel and the rate at which they are heated. The third stage of the gasification process is the gasification of the remaining char in which the solid matter in the fuel begins to chemically react with the water and other gases in the gasifier atmosphere. Finally, the fourth stage is a combustion stage where oxygen is supplied to the gasifier in order to provide the heat required for the gasification reactions.

Gasification of biomass typically occurs in either an entrained flow or a fluidized bed system. Each has its own distinct benefits and drawbacks. In an entrained flow gasifier, solid feedstocks are ground to a fine consistency and injected into the gasifier with water or steam and oxygen or air. The solid feedstock particle size is usually less than about 0.005 inch. There are generally no limitations on the feedstocks to an entrained flow gasifier, but high ash and high moisture feedstocks increase the oxygen consumption more than in other gasification types. Compared to other types of gasifiers, entrained flow gasifiers operate at high temperatures, have very low fuel residence times, and have high capacities. The very fine feedstock size needed for this type of unit makes it not well suited to biomass applications unless rigorous processing of the biomass is performed. Because this gasifier can operate at relatively high temperatures, the resulting syngas is largely free of tars and requires less downstream processing. Good experience has been gained at operating entrained flow gasifiers under conditions suitable for Fischer-Tropsch (FT) synthesis; namely, oxygen-blown and at high pressure. These process conditions reduce the downstream compression requirements and size of equipment.

In a fluidized bed gasifier, the feedstock is introduced near the bottom of the gasifier and is fluidized by the steam and oxygen (or air) feedstocks to the gasifier. Feedstock size is in the range of 1/4 to 1/2 inch, which is well suited for the use of biomass. Smaller particles will become entrained in the gas flow and will exit the gasifier before they have the chance to be gasified, resulting in poor carbon conversion. Typical residence times are on the order of minutes. Compared to entrained flow gasifiers, fluidized bed gasifiers operate at lower pressures and temperatures, have longer fuel residence times, and have lower capacities. While fluidized beds are much more common for biomass gasification, they produce a dirtier, lower quality syngas, and have not been widely demonstrated at the process conditions most suitable for FT production.

Regardless of the gasification system employed, the syngas must pass through a gas conditioning system to recover process heat and remove contaminants such as H_2S that foul downstream equipment and poison catalysts. Following gas conditioning, the syngas is catalytically converted to ethanol via a catalyst or genetically engineered microorganisms. Catalysts that can be used include modified Fischer-Tropsch catalysts, modified methanol catalysts, molybdenum sulfide catalysts, and others. Current catalytic processes produce a mixture of alcohols, requiring distillation and recycle systems to obtain the desired purity of ethanol.

The high temperatures and pressures associated with various portions of the gasification process and the downstream alcohol synthesis process require a significant level of thermal integration between these systems. Thermodynamically efficient process design is essential to the performance of the thermochemical ethanol process as a whole.

6.2.2.2 Gasification to Fischer Tropsch Diesel Processes

FT technology was originally developed in the 1920's, and has been commercialized in gas and coal to liquids facilities in Germany, Malaysia, South Africa, and Qatar. On the other hand, there are only a few projects utilizing or proposing to utilize biomass to FT liquids. The reason for this is primarily economic. The production of FT liquids via gasification is a complicated process. A large amount of high temperature and high pressure process equipment is required, meaning that only large scale projects with the lowest amount of feedstock or syngas processing will typically be economic. For this reason, most FT projects that have been proposed recently are based on the gasification of coal. US Department of Energy work has shown that without subsidies, the price of crude oil must be at least \$60 to \$85/barrel to support the economics of a large scale coal to liquids plant. For small-scale biomass plants, this number could be up to twice as high. Research performed in 2009 by the National Academy of Sciences showed a breakeven value of biomass to liquids plants at roughly \$125/barrel of crude oil.

While the economics of biomass to FT facilities are unfavorable versus large scale coal plants, biomass to FT does have some advantages. First, the lifecycle CO₂ emissions of biomass FT fuels are much lower than coal FT fuels. This will improve the economics if credits/debits for CO₂ are employed. Second, there are greater policy drivers and public acceptance of biomass FT relative to coal FT. The federal Renewable Fuel Standard provides incentives for future biofuel production. In addition, there is greater federal grant and loan guarantee opportunities available for second generation biofuel plants. Finally, the smaller scale that biomass FT plants would be designed at reduces the financial risk to potential investors.

For these reasons, there are a few projects, summarized in Table 6-1, either in-place or being developed for producing FT fuels from biomass. The following is a listing of companies developing or proposing biomass to FT facilities.

- Choren
- Oxford Catalysts
- Rentech
- Flambeau River/NewPage
- Stora Enso/Neste Oil
- FZK
- Velocys

6.2.2.2.1 Choren

Choren is located in Freiberg, Germany. Choren is the majority owner of the gasification technology known as the Carbo-V process. The Carbo-V process was developed specifically for biomass gasification and has been successfully demonstrated for diesel production using a Fischer-Tropsch back end. Choren has now or once possessed financial support from Shell, Daimler, and Volkswagen

In 2003, construction began on a 45 megawatt thermal (MW_{th}) prototype plant in Freiberg. Shell invested significant amounts of money in Choren and gave the company a license to the Shell

Middle Distillate (SMD) Fischer-Tropsch technology for diesel production. In 2008, Choren commissioned a 82,500 ton/year (225 ton/day) production facility that produces 4.6 million gallons per year of synthetic diesel.

Choren has designed their technology to be suitable on biomass feedstocks. All components of the system operate at low pressures. The biomass is fed to an indirectly heated, low temperature pyrolyzer where the feed is converted to a char and a pyrolysis gas. The pyrolysis gas is transported to the combustion chamber of the entrained flow gasifier and burned with oxygen to produce heat for the gasification of the char. The pyrolysis step in front of the gasifier allows for a wide variety of feedstocks (including municipal solid waste [MSW]), but adds cost to the technology.

While the system is flexible and well-suited for biomass Black & Veatch expects that the Choren Carbo-V gasification island will be an expensive system to build and operate. Factors that make the Carbo-V system so expensive include the fact that it is an entrained flow gasifier operating at high temperatures and low pressures. Although the low pressure saves the cost of manufacturing a pressure vessel, it also decreases the throughput, resulting in a lower output per volume of the gasifier. The low pressure operation also requires the use of syngas compressors to pressurize the syngas to the operating pressure of the downstream equipment and it increases the size of the equipment downstream of the gasifier and upstream of the syngas compressors.

6.2.2.2.2 Oxford Catalysts

Oxford Catalysts has recently developed an improved FT catalyst reactor employing a “microchannel” design that claims to improve FT liquids yields. This has the promise of improving the economics of small scale FT plants, such as those that would be produced from biomass, by increasing the rate of liquids production per ton of feedstock. In conjunction with the new reactor design, Oxford Catalysts has also developed a metal carbide based FT catalyst, which claims to be able to produce FT liquids at a lower temperature with longer catalyst life and greater liquids yield per ton of catalyst than currently commercial FT units. This would reduce the reactor size and yearly operating cost of the FT unit, which would be beneficial for biomass based FT systems. Oxford has partnered with large development engineering firms in Asia and Europe, and plans to start-up a 10,000 gallon per year demonstration plant in 2010.

6.2.2.2.3 Rentech

Rentech has plans to open a biomass FT facility in California. Rentech announced in 2009 its plans to develop a plant in Rialto, California, that would produce an estimated 600 barrels per day of product along with 35 MW of power. Rentech would utilize the SilvaGas gasification technology, a circulating fluidized bed design which was commercially demonstrated at the 400 ton per day scale from 1998 to 2001 in Burlington, Vermont. Upgrading technology developed by UOP plans to be utilized on-site to produce fungible distillate fuels. The feedstock for this facility is expected to be local woody green wastes for which it is expected that Rentech will receive a tipping fee. It is very likely that this fee will be critical to the economic development of the project. The projected start-up date for this project is 2012.

6.2.2.2.4 Flambeau River/NewPage

Two biomass to liquids plants were announced in Wisconsin in 2009. Both the Flambeau River Biofuel and the New Page projects plan to use a pulse gasifier developed by ThermoChem Recovery International and FT catalysts from Emerging Fuels Technology. These projects range from 6 to 18 million gallons of FT products per year. These plants are not projected to start-up until 2012 at the earliest.

6.2.2.2.5 Stora Enso/Neste Oil

A biomass FT demonstration unit opened up in Finland in 2009 as a joint venture between a pulp and paper company (Stora Enso) and a refinery (Neste Oil). This is a small-scale unit, using Foster Wheeler fluidized bed gasification technology and upgrading units at a nearby Neste refinery.

6.2.2.2.6 FZK

Commercialization efforts are also being undertaken to produce FT fuels from pyrolysis oils. A consortium of Lurgi, Air Liquide, and the University of Karlsruhe (Germany), are developing a pilot plant in Germany to demonstrate the “Bioliq” process. This process consists of fast pyrolysis of biomass, followed by oxygen-blown, entrained flow gasification, then cleaning and conversion of the syngas to liquid fuels. This pilot plant is projected to start-up in 2011.

6.2.2.2.7 Velocys

Velocys, the US-based subsidiary of UK synthetic fuel developer Oxford Catalysts Group, recently developed a Microchannel Technology that can be applied to a Fischer-Tropsch process. The F-T reactors using Velocys Microchannel Technology have parallel arrays of microchannels, with typical dimensions in the 0.1 to 5.0 mm range. These microchannel arrays, which are multiple reactors manifolded in parallel, can accelerate a F-T process 10 to 1,000 fold by reducing heat and mass transfer distances, which reduces the heat and transfer resistance between the process fluids and channel. This Microchannel Technology could improve the performance of the exothermic chemical processes while reducing the size of the chemical reactors by 10 fold, thus saving the capital cost of F-T synthetic fuel production (Tonkovich et al., 2009). A F-T biomass-to liquids demonstration plant using Microchannel Technology was built in Austria and has been running since July 2010. The demonstration plant is already producing over 0.75 kg of high quality FT liquids per litre of catalyst per hour – 4 to 8 times greater productivity than conventional systems.

Besides the Choren facility, none of the other units have been built or are close to development at the commercial scale. This has to do both with complexity and cost. Stand alone biomass to FT units are not economically competitive versus petroleum based transportation fuels without significant funding support and very inexpensive feedstocks. In addition, the process requires utilization of technology that has not been widely commercialized in this application, and which requires integration into an established infrastructure that is not highly engaged in the process.

In evaluating the projects underway or being considered, a number of factors need to be considered in the development of biomass to FT. First, government or large private industry support is needed to provide the capital and financing support. Second, having low cost feedstocks, such as woody wastes at the Rentech plant, are very helpful to improve the financial performance of the facility. Locating biomass to FT units in places such as California that have high prices for waste diversion could be attractive. Finally, partnerships with established players in the petroleum refining industry such as Shell, UOP, and Neste Oil, have been making worthwhile advances in biomass to FT technology.

6.2.2.3 Gasification to Methanol, Dimethyl Ether, and Methanol to Gasoline Processes

Another route considered for the development of fungible transportation fuels from biomass is production of methanol and methanol derivatives, such as Dimethyl ether (DME) and “green gasoline” from a methanol intermediate. The process used in synthesizing these chemicals is similar to the biomass to FT route in that gasification and syngas cleaning is first employed.

The production of methanol from syngas is a well understood, commercial process. Most of the world’s industrial methanol is made from syngas derived from auto thermal reforming of natural gas. A copper/zinc catalyst is used under high pressure (800 to 1200 psi) and temperatures (500 °F). While a few other alcohols and chemicals are produced, the yield is more than 90 percent methanol. Like the FT reaction, this reaction is very exothermic and requires careful reactor design to remove the process heat.

Methanol production and demand has continued to increase throughout the last decade. Seven methanol plants with capacities of 600 million gallons or more began operation between 2004 and 2007 (Dolan, 2008). Many of these facilities were located in areas where there was access to cheap natural gas, such as Trinidad and Tobago, Chile, Venezuela, and Equatorial Guinea. Methanol can also be produced from coal, and the coal-based methanol production has expanded considerably in China.

After synthesis, the methanol can be fed, in a gaseous phase, into a DME or a methanol-to-gasoline (MTG) reactor, or it can be used directly as a fuel.

For DME synthesis, the methanol vapor is fed to a DME reactor. The catalyst in this reactor is an activated alumina that dehydrates the methanol into a mixture of DME, methanol, and water. If desired, the reaction can be stopped at this step, with the gas cooled, condensed, and separated into its main constituents. DME is a vapor at room temperature, so it must be stored under pressure or in a gas tank.

As an alternative to this two-step process for DME production (syngas to methanol, followed by methanol to DME), researchers are investigating a one-step process to convert syngas directly to DME. Focus is on a reactor system with a “bifunctional” catalyst that can perform both the syngas to methanol and methanol to DME reactions in the same process vessel. The two different catalysts that perform these steps are combined together. The challenge is developing appropriate catalyst formulations, ratios, arrangements, and reaction conditions. Conventional methanol synthesis and dehydration catalyst routes are typically used, with recent successes reported in

doping the methanol catalyst with zirconium and gallium (Kang et al., 2010). Both fixed and slurry bed reactors have been explored to perform this one-step process, although novel research has recently been performed using fluidized beds with liquid sorbents for DME removal.

Four companies are currently investigating one-step DME production: Haldor Topsoe (Denmark), JFE (Japan), Kogas (Korea), and Unitel (USA). The research is currently in the pilot stage, with no commercial facilities expected to be completed before 2013.

The development of DME production and using DME as an alternative transportation fuel has been promoted by the Chinese government over the past decade. The growth of the DME industry in China is due to the fact that China has enormous coal reserves and coal is the primary feedstock used to produce DME. DME, as an energy source, was first introduced in China to replace LPG for household use. China is now the leading DME producer in the world. In 2002, the annual capacity of DME in China was only 31,800 tons. With the rising price of traditional petroleum fuel, many DME production plants were built and China's DME production surged to 2.2 million tons in 2007. To prevent over-investment into DME projects, the Chinese government now only approves those plants with an annual DME production scale of one million tons or more. Yet, it is expected that DME production in China will reach 15.8 million tons in 2010, and 20 million tons by 2020, most for transportation applications (Shanghai Daily, 2008).

Recently, researchers from Shanghai Jiao Tong University and Xi'an Jiao Tong University have developed buses powered by DME. In 2006, several DME bus line demonstration projects were carried out in Shanghai and the Shandong province to evaluate the feasibility of DME as a transportation fuel. Meanwhile, the world's first commercial DME filling station was built in Shanghai to supply the bus line. The Shanghai government planned to deploy 1,000 DME powered buses in 2010 (Shanghai Daily, 2008).

Japan is also working hard to promote DME production and DME vehicles. The Japan DME Ltd built a DME production pilot plant and carried out a feasibility study for production of 5,000 t/day in 2006. More recently, a group named DME Promotion Venture, including MGC, ITOCHU, JAPEX, Taiyo Oil, Total, etc, established a joint venture to develop a DME production plant with a capacity of 80,000 ton (Ohno, 2007). With financial support from the Japanese government, a number of diesel vehicle manufacturers, like Nissan Diesel, Hino Motors, Isuzu, and Mitsubishi Motors, have been developing DME-fueled heavy duty vehicles (Bourg, 2006). In addition, Volvo in Sweden has been actively developing bio-DME vehicles. Volvo Trucks conducted multiple comprehensive customer-based field tests using bio-DME in 2007. Between 2010 and 2012, Volvo, partnered with the EU, the Swedish Energy Agency, fuel companies and the transport industry, to test 14 Volvo FH trucks powered by bio-DME at four locations in different parts of Sweden to investigate the potential for full-scale investment in Bio-DME as a transportation fuel. DME refueling stations will be built by a fuel company called Preem to support the demonstration project (Volvo website 2010). The goal of this project is to demonstrate the full range of technologies that would be used for Bio-DME from fuel production, distribution and refueling, to the fuel utilization.

Methanol can be fed directly to an MTG reactor if directly blendable gasoline components are desired. A zeolite catalyst commonly used in the petroleum refining industry (ZSM-5, consisting

largely of aluminum and silicon oxides) is employed for the synthesis of gasoline. One major advantage that this process has over the FT process is the very high level of conversion and selectivity for fungible hydrocarbons. The MTG reactor produces a stream of roughly 50 percent water and 50 percent hydrocarbons, with 80 to 90 percent of the hydrocarbon stream consisting of components suitable for gasoline blending. No diesel or jet fuel is made in the reactor.

The hydrocarbons from this arrangement require much less processing when compared to FT liquids; very light hydrocarbons must be fractionated, and 3 to 6 percent of the stream is a component (durene) that is a solid at typical storage conditions and may need to be isomerized. Much of the gasoline produced is suitable for on-road use, although fractionation and blending with other streams would be the most economic step. The fuel has zero sulfur, similar to FT liquids. The aromatics content of the gasoline is in the mid 20 percent range, which meets most state on-road standards, including those for the California ARB.

The MTG process was developed and patented by Mobil in the 1970's. Due to the commercial status of methanol catalysts, high yield of fungible products, and insights gained from commercial deployment of MTG units, the technology should be considered fairly mature. Incremental improvements on the process have been obtained from the operation of a commercial natural gas to MTG facility that was operational in New Zealand from 1985 to 1996. The facility was shutdown largely due to the low price of petroleum-based substitutes.

In the United States, there have been proposals to develop MTG facilities. The development company DKRW has proposed a large coal to gasoline project using MTG technology in Wyoming. This project was originally developed to produce FT liquids, but has since changed its synthesis route. Synthesis Energy Systems (SES) has developed license agreements with ExxonMobil for use of the MTG technology throughout the world, with a coal to gasoline project briefly considered in West Virginia in 2008. SES is largely focusing on projects in China at this time, with methanol or DME the main product.

There are no commercial biomass gasification to methanol or gasoline via the MTG process facilities being developed at this time, although biomass-based DME routes are being strongly considered. The lack of commercial facilities is largely due to the economy of scale issue that hampers the economics of small-scale plants running on biomass when compared to the proposed scale of coal or petroleum coke gasification projects. All solid biomass-based projects for these products are largely at the laboratory or demonstration scale. Exelus of Livingston, New Jersey, was recently awarded a US DOE grant for further development of their biomass to gasoline project. Projects like this, specifically for biomass, are needed to advance this route for transportation fuels. Chemrec in Sweden is currently developing a biomass to DME project that will gasify black liquor, a liquid by-product of the pulp and paper industry. Because of the poor economics of "typical" biomass to DME or MTG plants, very specific, niche applications where the use of the technology may be attractive must be sought.

6.2.2.4 Production of Cellulosic Ethanol via Gasification

Although a small number of facilities are believed to be under construction, there are no commercial thermochemical cellulosic ethanol facilities currently in operation in the United

States. Relative to the number of companies attempting to develop biochemical projects, there are a smaller number of companies developing thermochemical ethanol projects in the United States. However, each of the leading thermochemical companies has announced specific plans to develop commercial-scale facilities in the near- to mid-term. Some of the key companies working to develop (or who possess) the required thermochemical technology required to install commercial-scale thermochemical cellulosic ethanol facilities include:

- Coskata (Coscata, 2010)
- INEOS New Planet Bioenergy (INEOS, 2010)
- Range Fuels (Range Fuels, 2010)
- Fulcrum Bioenergy (Fulcrum Bioenergy, 2010)
- Enerkem (Enerkem, 2010)

6.2.2.4.1 Coskata

Established in 2006, Coskata was formed to commercialize concepts initially developed at Oklahoma State University and the University of Oklahoma. The process employed by Coskata combines thermochemical and biochemical processes: gasification technologies are employed to convert solid biomass into syngas, and anaerobic microorganisms are utilized to synthesize syngas-derived ethanol.

Because the gasification process breaks down the solid biomass and the microorganisms utilized by Coskata consume syngas rather than sugars, the Coskata process eliminates the need for pretreatment enzymes, which are a costly component of biochemical processes. Furthermore, the microorganisms do not require the high temperature and pressure environment required by catalytic synthesis processes, avoiding large energy inputs to the system.

In October of 2009, Coskata began operation of a demonstration-scale facility in Madison, Pennsylvania. This facility, with a production capacity of 40,000 gallons per year, is located at the Westinghouse Plasma Center, the site of the Westinghouse's pilot-scale plasma gasification system. The use of plasma gasification systems allows for the Coskata systems to process a wide variety of biomass feedstocks including woody biomass, agricultural residues, energy crops and construction wastes. Coskata claims that the facility is a demonstration of "minimum scale engineering," which means it is the smallest size that will still allow the company to scale directly to 50 MGY or 100 MGY commercial facilities. The company anticipates that its first 50 MGY will be commercially operating by the end of 2012 (Coscata, 2009).

6.2.2.4.2 INEOS New Planet Energy

INEOS New Planet Energy, a joint venture between British chemical company, INEOS and renewable energy developer, New Planet Energy, was formed in 2009 to develop a cellulosic ethanol production facility. The facility will produce ethanol from organic wastes, including wood residues, yard wastes and vegetative wastes.

In 2008, INEOS acquired the cellulosic ethanol technology developed by Bioengineering Resources Inc. (BRI), based in Fayetteville, Arkansas (INEOS, 2008). In the BRI process,

syngas is produced by the gasification of organic waste or other organic material. Syngas exits the gasifier at temperatures up to 1,300°C. However, the gas must be cooled to approximately 40°C before it can be introduced to the fermentation reactor. The syngas undergoes a heat recovery/gas cleaning step, with the waste heat used to generate high pressure steam to drive steam turbine generators. Following gas clean up and heat recovery, ethanol is produced through the anaerobic fermentation of the syngas. Distillation and separation processes are used to increase the quality of the ethanol to fuel grade.

INEOS New Planet Energy intends to locate its demonstration facility near Vero Beach, Florida. Current plans call for the facility to initially produce 8 MGY of ethanol from organic wastes. In addition, the facility will generate 2 MW of excess renewable power that may be sold to the grid. If successful, INEOS New Planet Energy intends to expand the facility to produce 80 MGY. The initial 8 MGY facility is expected to be operational by the end of 2011. INEOS New Planet Energy has also been awarded up to \$50 million from the US DOE for the construction of the project (TCPalm.com, 2009; INEOS, 2009).

6.2.2.4.3 Range Fuels

Range Fuels is privately funded by venture capital firm Khosla Ventures LLC to develop processes for the commercial production of ethanol from biomass. The company has developed the two-stage K2 process to thermochemically produce ethanol from a wide range of biomass feedstocks.

In the initial step of the K2 process, biomass is converted into gas under heat, pressure and steam in a Pyrolytic Steam Reforming Gasifier (PSRG). The PSGR utilizes a Staged Temperature Reaction Process (STRP) to improve conversion efficiency and virtually eliminate the tars typically produced in thermochemical conversion processes. Gas entrained biomass passes through the devolatilization reactor which raises the temperature of the incoming materials up to 230°C. At this temperature, a substantial portion of the oxygen is consumed as the more reactive fraction of the biomass undergoes devolatilization. The temperature of the feed continues to increase until it combines with steam super-heated to approximately 815°C. The result is the production of syngas with substantial fractions of CO and H₂. Finally, the syngas passes over a proprietary catalyst and produces a mix of alcohols including ethanol, methanol, propanol and butanol. The products are processed to maximize the ethanol yield and then separated.

Currently, the first commercial installation of the K2 process is under construction near Soperton, Georgia. Range Fuels broke ground on this facility in November of 2007, which plans to produce 25 MGY of ethanol from wood waste and forest residues. If operations are successful at the initial 25 MGY scale, this facility may be expanded to produce 100 MGY of ethanol. Range Fuels was awarded a \$76 million grant from U.S. DOE to assist with the development of the Soperton facility. In addition, the U.S. DOE has also provided loan guarantees worth \$80 million to the project. Range Fuels anticipates that the facility will begin commercial operations in 2010 (Range Fuels 2007, Range Fuels, 2009).

All of the companies listed above intend to commission commercial-scale facilities ranging in size from 50 to 100 MGY in the next 2 to 5 years. Each of these companies possesses processes

that may be capable of producing ethanol from cellulosic biomass. All employ gasification as an initial step. Because gasification processes are employed, it is reasonable to assume that a variety of biomass feedstocks, including MSW, may be utilized as feedstocks for these processes. Range Fuels would employ catalytic synthesis of alcohols, while Coskata and INEOS New Planet Energy would employ microorganisms that can biologically convert syngas to ethanol.

Like the companies developing biochemical ethanol processes, it is likely that financial strength and ability to manage the construction and commissioning of initial facilities will determine, in part, the eventual commercial success of these companies. While the primary thermochemical ethanol technologies (i.e., gasification processes and catalytic chemical synthesis) have been technically proven, it remains to be demonstrated that the integrated systems are capable of producing ethanol from biomass feedstocks in a manner that is economically competitive with conventional fuels (i.e., gasoline and conventional diesel).

6.2.2.5 Renewable Jet Fuel via Gasification

The airline industry is facing an initial carbon liability of \$1.53 billion in 2012 when aviation enters the European Union's Emission Trading Scheme in 2012 (Lane, 2010). "Among top airlines, British Airways, United and Delta will all have exposures in excess of 3 million metric tons of CO₂, and face offset payments of more than \$50 million each." Biofuels are one potential method of addressing this issue, and the airlines are making a major push to have a renewable jet fuel receive ASTM and FAA certification in 2010. For aircraft, the only realistic biofuels option is to have a renewable fuel that is as close to existing petroleum based jet fuel as possible. In this section, the development of jet fuel via gasification followed by Fischer-Tropsch processing. Additional information related to the production of jet fuel via hydrotreatment of oils and fats is provided in Chapter 8. There are a number of companies engaged in the development of production facilities and commercial arrangements for renewable jet fuel, as discussed in the following. The information below is summarized from Lane (2010).

A summary of projects that are on-going with the military, the airline industry, or airport facilities are described below:

- The US Air Force will construct a \$2.5 million Assured Aerospace Fuels Research Facility at Wright-Patterson Air Force Base in Ohio. The facility is expected to be completed in the summer of 2010 and is expected to produce and develop 15 to 25 gallons of coal, biofuels, and other gas alternatives every day.
- Accelergy Corporation, a Houston-based company, recently constructed a pilot plant at the Energy & Environmental Research Center (EERC) at the University Of North Dakota, and started to produce a synthetic jet fuel from coal and biomass. This fuel is being evaluated by the United States Air Force (USAF) as the industry benchmark for 100% synthetic jet fuel (Accelergy Website, 2010). Accelergy is the first company to provide 100% synthetic jet fuel that can meet the JP-8 standards. Their process is different from a traditional Fischer-Tropsch process that requires turning coal or biomass into a synthetic gas and then converting the gas into a liquid. Accelergy's integrated Coal-Biomass to Liquids (CBTL) process utilizes a proprietary micro-catalytic liquefaction technology and direct biomass conversion technologies developed by Exxon-

Mobil Research and Engineering Company in 1970s to produce synthetic jet fuel. During the process, a slurry of pulverized coal is mixed with hydrogen and a proprietary catalyst under high temperatures and pressures. The gas products from the coal, which are within the petroleum distillate, can then be synthesized into a synthetic jet fuel.

- British Airways will construct a 19 mgy waste biomass gasification plant at a site in East London. The plant will commence operations in 2014 using the Fischer Tropsch process to convert 500,000 tons of waste biomass to jet fuel.
- Qatar Airways, Qatar Science & Technology Park, Qatar Petroleum and Airbus are working together to prepare a detailed engineering and implementation plan for economically viable and sustainable biofuel production, a biofuel investment strategy, and an advanced technology development program. In October 2009, Qatar successfully conducted the first commercial flight powered by a Gas-to-Liquid fuel blend.
- In January 2010, Stockholm's Arlanda Airport completed a formal feasibility study of a biofuels project to supply the airport with 15 Mgy of renewable jet fuel, or 10 percent of the airport's annual consumption, with a reduction in carbon emissions of 150,000 tonnes per year. The project plans to use the Fischer-Tropsch process to convert woodchips and other forest residues to biofuels. Two facilities are planned, one to produce jet biofuel and the second to produce an intermediate F-T synthetic oil that can be upgraded to jet fuel. The total cost is estimated to be \$1.789 billion and will be competitive with \$100/bbl oil.

A summary of other projects that are on-going related to specific facilities or technologies are described below:

- Rentech has a demonstration plant in Commerce City, Colorado producing synthetic jet fuel and renewable diesel. Rentech is constructing a plant in Rialto, CA that will utilize urban yard and woody green waste to produce ultra clean renewable fuels. The plant is designed to produce 600 barrels per day of synthetic fuel as well as 35 megawatts of renewable power. Rentech has signed an agreement with 13 airlines for renewable, drop-in jet fuel made from waste biomass.
- TRI, Rentech, Velocys, Choren, Flambeau River Biofuels/Johnson Timber, AP Fuels and World GTL among other companies have banded to form the Low Carbon Synthetic Fuels Association to represent the biomass to liquid fuel industry using the Fischer-Tropsch process to produce synthetic renewable diesel and renewable jet fuel. The Association will focus on lobbying for advanced biofuels, and have received support from the Outdoor Power Equipment Institute, Auburn University, Audi America, Chemrec AB, Mercedes Benz USA, Pacific Renewable Fuels, Renewable Energy Institute International, and Volkswagen in comments delivered to the EPA on the importance of advanced drop-in biofuels that do not require infrastructure changes.
- Clear Fuels Technology and Hughes Hardwood have a memorandum of understanding (MOU) to develop a renewable jet or diesel fuel biorefinery co-located with Hughes Hardwood's wood component manufacturing facility in Collinwood, TN. Hughes will supply 1000 dry tons per day of wood products which can be converted into ~16 million gals/yr of synthetic jet or diesel, ~4 million gals/yr of naphtha, and ~8 megawatts of power. The project is expected to start production in 2014.
- Dynamic Fuels is expected to open a commercial-scale facility in Louisiana to manufacture up to 75 million gals per year from waste biomass.

- The Energy & Environmental Research Center (EERC) at the University of North Dakota has a strategic partnership with Accelergy Corporation to commercialize a suite of technologies for the production of liquid fuels from coal and biomass (Accelergy, 2010). Accelergy will license the EERC developed biomass conversion process technology from the EERC Foundation as part of Accelergy's coal-biomass-to-liquid (CBTL) process (licensed from ExxonMobil Research and Engineering Company) to accelerate the development of specialty liquid jet fuels used by the military from cleaner, nonpetroleum sources. This follows a mandate by the U.S. Air Force (USAF) to procure 50% of its fuel from cleaner and domestic sources by 2016.
- In February 2010, Bye Energy acquired Novare Biofuels rights to a thermochemical, cellulosic biomass process concept and design to produce both aviation gasoline and aviation jet fuel.

6.2.2.6 Production Requirements

Since gasification and the associated processes to produce a liquid fuel are complicated, it is useful to examine the different elements and requirements associated with these processes. The high temperatures and pressures associated with various portions of the gasification process and the downstream synthesis processes require a significant level of thermal integration between these systems. Thermodynamically efficient process design is essential to the performance of the thermochemical ethanol process as a whole. In addition, the appropriate H_2/CO ratio must be obtained to achieve appropriate synthesis conditions in the different types of downstream reactors. For a FT catalyst, this will typically vary from less than 1 to 2.5. A water-gas shift reactor is usually employed to obtain the ratio desired.

The syngas produced from a gasification process must pass through a gas conditioning system to recover process heat and remove contaminants such as H_2S that foul downstream equipment and poison catalysts. The main components that must be removed include the following:

- Particulates: Can cause corrosion and poor quality fuels, but are fairly easily removed with cyclone, filters, and/or scrubbing equipment.
- Tar: Tar formation (high molecular weight compounds of benzene) from biomass gasification is a common problem that will require removal or cracking to prevent downstream fouling. Tar removal or destruction remains one of the most challenging cleaning steps associated with biomass gasification.
- Sulfur Compounds: Sulfur compounds, namely H_2S , are poisons to the FT catalyst. These can be removed using conventional processing equipment.
- Ammonia
- Metals and Chlorides

For a FT process, a range of hydrocarbons is produced, so further processing is necessary to break the products into materials that can be used for on-road transportation fuels. This largely entails filtering and recycling any entrained FT catalyst, cracking waxes and heavies into lighter products, and distillation to separate the different boiling point materials. The diesel fuel produced is of excellent quality and can be used in neat blends directly into compression ignition engines. It has zero sulfur, high cetane, and typically superior environmental performance

relative to conventional diesel fuel. The gasoline boiling range material (naphtha) has a low octane level due to the large amount of paraffins present. It could be used as a chemical plant feedstock or gasoline blending material, but is not suitable for neat blends. The jet fuel will typically meet all ASTM jet attributes with the exception of pour point (cold flow properties). Because of this, FT jet will need to be blended with other materials to meet aircraft specifications.

The hydrocarbons from a MTG arrangement require much less processing when compared to FT liquids. Very light hydrocarbons must be fractionated, and 3 to 6 percent of the stream is a component (durene) that is a solid at typical storage conditions and may need to be isomerized. Much of the gasoline produced is suitable for on-road use, although fractionation and blending with other streams would be the most economic step. The fuel has zero sulfur, similar to FT liquids. The aromatics content of the gasoline is in the mid-20 percent range, which meets most state on-road standards, including those from CARB.

NREL conducted a study to examine the requirements and performance of thermochemical ethanol processes that provides a perspective on different processing elements. This study assumed that 2,200 dry tons per day of woody biomass would be converted to syngas within a dual-reactor, indirectly-heated, steam gasification system.¹ Following syngas cleanup and conditioning, the facility modeled by NREL would employ a modified Fischer-Tropsch catalytic process to produce ethanol and higher alcohols (Phillips et al., 2007).

As its baseline case, the NREL study assumed that the facility would be integrated with heat recovery systems, utilizing a portion of the syngas produced by the gasification process to generate process heat. The utilization of syngas for process requirements eliminates the consumption of natural gas or other fossil fuels, but also diminishes the quantity of ethanol produced by the facility. As an alternate case, the facility could maximize the production of ethanol by converting all generated syngas to alcohols and firing natural gas to supplement energy recovery. In the “Self-Sufficient” scenario, the thermochemical facility modeled by NREL processes 2,200 tons of biomass per day to produce roughly 175,000 gallons of ethanol per day. In the alternative “Supplemental Natural Gas” scenario, the thermochemical facility processes 2,200 tons of biomass per day to produce roughly 240,000 gallons of ethanol per day. The relevant performance parameters of these scenarios are provided in Table 6-2.

¹ The gasification system modeled in the NREL study is composed of a low-pressure circulating fluidized bed (CFB) gasification reactor coupled with a low-pressure CFB combustor. The operational parameters of the system were modeled based on correlation with empirical data obtained on a 9 ton per day test facility located at Battelle Columbus Laboratory.

Table 6-1: Performance Characteristics for a Thermochemical Ethanol Facility.

Parameter	Self-Sufficient Scenario	Supplemental Natural Gas Scenario
Biomass consumption (dry ton/day)	2,200	2,200
Natural gas consumption (MW, LHV)	0	115 ^a
Ethanol yield (gallons/dry ton of biomass) ^b	80	110
“Other” Alcohol yield ^c	14	15
Ethanol production (million gallons/year) ^{b, d}	62	85

Source: Phillips et al., 2007. Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. NREL/TP-510-41168.

Notes:

^a Calculation of required natural consumption required for external cogeneration case based on gasifier efficiency (LHV basis) of 76.1% and utilization of 28% of the raw syngas for internal electrical and process steam in syngas cogeneration case.

^b The NREL study modeled a process that would employ a dual-reactor, indirectly-heated, steam gasification system and Fischer-Tropsch processes to produce a mix of alcohols.

^c “Other” alcohols include: methanol, propanol, butanol, pentanol and higher alcohols.

^d Assumes 8,406 hours of operation per year.

It is important to note that the system modeled by NREL utilizes process efficiencies that exceed currently demonstrated results. Specifically, improvements in the conversion of hydrocarbons and ammonia in the catalytic tar reformer, and improvements in process conditions and performance for alcohol synthesis catalysts, are anticipated by the modeled system. The specific improvements assumed in modeling of tar conversion are presented in Table 6-3, while specific improvements assumed in modeling of alcohol synthesis processes are presented in Table 6-4.

Water requirements for the process modeled by NREL are primarily associated with the operation of the cooling tower, with the balance of the water requirements attributed to boiler feedwater makeup. The total water consumption for the system is less than 2.0 gallons per gallon of ethanol production, which compares favorably to the water requirements of conventional ethanol processes (typically in the range of 2.5 to 5.0 gallons of water per gallon of ethanol production).

Table 6-2: Process Improvements Assumed for Catalytic Tar Conversion.

Compound	Experimental Conversion to CO & H₂*	Target Conversion to CO & H₂
Methane (CH ₄)	20%	80%
Ethane (C ₂ H ₆)	90%	99%
Ethylene (C ₂ H ₄)	50%	90%
Tars (C ₁₀₊)	95%	99.9%
Benzene (C ₆ H ₆)	70%	99%
Ammonia (NH ₃)	70%	90%

Source: Phillips et al., 2007. Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. NREL/TP-510-41168.
Notes: * Phillips et al., 2004. Preliminary Report on the Performance of Full Stream Tar Reformer. Internal NREL Milestone report.

Table 6-3: Process Improvements Assumed for Mixed Alcohol Synthesis.

Parameter	“State of Technology” Conditions	Target Conditions Used in NREL Process Design and Aspen Model
Temperature (°C)	~ 300	300
Pressure (bar)	103 – 138	69
H ₂ /CO ratio	1.0 – 1.2	1.0
CO ₂ concentration (mol%)	0% – 7%	5.0%
Sulfur concentration (ppmv)	50 – 100	50

Parameter	“State of Technology” Conditions	Target Conditions Used in NREL Process Design and Aspen Model
Total CO conversion (per pass)	10% – 40%	60%
Total alcohol selectivity (CO ₂ -free basis)	70% – 80%	90%
Gas hourly space velocity (hr ⁻¹)	1,600 – 12,000	4,000
Catalyst alcohol productivity (g/kg-catalyst/hr)	150 – 350	600

Source: Phillips et al., 2007. Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. NREL/TP-510-41168.

In addition to the oils, lubricants and spare parts required of any mechanical facility, the thermochemical system considered by NREL requires consumable materials for the gasification system, the gas conditioning systems, the alcohol synthesis system, and the steam cycle equipment. Consumable materials required for operation include:

- Gasifier bed material
- Tar reformer catalyst
- Sulfur removal system chemicals
- Alcohol synthesis catalyst
- Water treatment chemicals

For alternative system configurations, some of the consumable materials mentioned above may not be required. For example, thermochemical processes that employ entrained flow gasifiers require neither bed material makeup nor tar reforming catalyst. Water treatment chemicals may not be required if a facility is able to purchase electricity and process steam. Chemicals associated with sulfur removal and catalysts for alcohol synthesis likely will be required for all thermochemical ethanol production processes.

Thermochemical processes also produces CO₂ emissions (as well as lesser quantities of NO_x, SO_x, and CO), derived primarily from the generation of required electricity and process steam. Additional CO₂ emissions may be generated from the regeneration of tar reformer catalysts and operation of sulfur removal systems. Similar to the biochemical process, it should be noted that for the “Self-Sufficient” scenario (in which a portion of the biomass feedstock is used to generate electricity and process steam), the majority of CO₂ emissions are derived from a renewable resource, rather than fossil fuel.

6.2.3 *Distribution and Utilization of Transportation Fuels from Gasification Processes*

6.2.3.1 Distribution and Utilization of Fischer-Tropsch Fuels

Since F-T diesel is a synthetic diesel fuel, it can be used to replace petroleum diesel without modification of the vehicles and refueling infrastructures. F-T diesel has low sulfur levels, a high cetane number, low density, and very good flow properties (Waterland, 2006), resulting in reduced emissions and good engine performance. As mentioned above, F-T diesel has very similar properties to conventional diesel; the distribution of F-T diesel would not require new or modified pipelines, and storage tanks. A lubricity additive is typically used with F-T diesel to prevent excessive wear of fuel injectors and other related parts. Currently, F-T diesel is usually used as blendstock for petroleum diesel. The cost of distribution of F-T diesel blends would be similar to that of petroleum diesel.

6.2.3.2 Distribution and Utilization of DME

DME has a number of unique characteristics, so vehicles must be modified to use it as a transportation fuel. DME is a gas at ambient pressure and temperature (like LPG), and the liquefied DME fuel has extremely low lubricity and low viscosity. As a consequence, the fuel injection system for DME must be able to handle high vapor pressure, high compressibility, and low viscosity (Hansen and Mikkelsen, 2001). In addition, DME is not compatible with most of the elastomers and may dissolve the elastomers in the engine and fuel delivery system after prolonged exposure due to its corrosiveness. Further, the energy content of DME is about 65% of petroleum diesel, meaning the size of fuel storage tanks in the vehicles has to be enlarged for a DME vehicle to have a range comparable to a traditional diesel vehicle. Presently, DME vehicles

have only been developed at a demonstration level, and currently no commercial DME vehicles are available (Hansen, 2001; Bourg, 2006). DME has similar properties to LPG, and it can be handled and distributed using methods similar to those required for LPG, and with some of the LPG infrastructure. The distribution of DME can follow the platform of transporting LPG using ocean-based and land-based LPG infrastructures. Existing LPG refueling stations can be converted to DME refueling stations with minor modifications to the pumps, seals, and gaskets (Semelsberger et al., 2006), although currently there are only 2420 LPG refueling stations in the US and 158 stations in California.

6.2.3.3 Distribution and Utilization of Methanol

The use of methanol in vehicle applications has some of the same limitations as those of ethanol, but the number of methanol vehicles and associated infrastructure is considerably less developed than that for ethanol fuels. Methanol has a lower energy content than either ethanol or gasoline, which results in increased fuel consumption. Methanol is less volatile than gasoline and burns at a lower temperature, making engine starting in cold weather more difficult. Methanol also has solvent properties that make it more corrosive than gasoline or ethanol. This includes issues with unprotected aluminum and other metals, elastomers and seals, including materials such as rubber and polyurethane.

Interest in the use of methanol for a transportation fuel gained impetus in the 1970s in response to oil shortages. The State of California, as part of its Methanol Fuel and Vehicle Program, ran an experimental test program over the course of the 1980s and 1990s to evaluate the potential of methanol-fueled vehicles. This included dedicated methanol (M100) vehicles and flexible fuel vehicles designed to run on mixes of up to 85% methanol with gasoline. A summary of some early methanol demonstration programs is provided in Nichols (2003) and Ward and Teague (1996). The California program involved demonstrations with over 900 vehicles of 16 different models operated by 90 participating fleets, and led to development of commercially available methanol/gasoline vehicles from Ford, General Motors, and Chrysler (MacDonald, 2005). Between 1987 and 1999, over 17,000 methanol FFVs and hundreds of transit buses and school buses were sold in California (Dolan, 2008).

These early programs had some success with the use of methanol fueled vehicles, but over the years the use of methanol and deployment of methanol-fueled vehicles has declined significantly. A number of factors contributed to the significant decline in methanol fuel use, including a growth in interest in natural gas fueled vehicles air quality improvement, the discontinuation of the California's methanol program, and a growth in the ethanol industry due to support in the farming community and government subsidies (Nichols, 2003; MacDonald, 2005). There are currently no production M100 or M85 vehicles, although several thousand of these vehicles may still be in use in California (MacDonald, 2005). A network of 60 public retail stations and 45 private fleet stations was put in place in California during the time of its Methanol Fuel and Vehicle Program (Dolan, 2008). It is not certain how many of these stations remain in use at this point, and the Alternative Fuels & Advanced Vehicle Data Center (DOE 2007d, AFAVDC, 2009e) is not maintaining records relating to methanol stations, as it does for the other alternative fuels.

Methanol use has grown in China (Dolan, 2008; Lynn, 2009). M-15 has been used at varying levels throughout the Shanxi Province since 2003. M-100 has also been used in demonstrations in 200 buses and 1,000 taxis in Shanxi Province. Chery Automobile, China's fastest growing independent automobile manufacturer, conducted a demonstration with 20 methanol FFVs and is now ready for full-scale production. Shanghai Automotive Industry Corporation, one of the 3 big automakers in China, is also developing a number of methanol-fueled cars. Other Chinese automakers that have been developing methanol-fueled cars include Shanghai Maple Automobile, Chang'an, Greely Automotive, and Huapa Automotive.

6.2.3.4 Distribution and Utilization of Renewable Jet Fuel from Gasification

For jet fuels, the current jet specification does not allow co-processing of bio-based materials through current refining systems (ASTM, 2007, 2009, 2010). The spec only allows petroleum based crudes or FT syngas (as surrogate for crude from any source) to be feedstocks for jet. Currently, co- or dedicated processing of non-conventional sources is only allowed via a separate approval and the specification being modified to reflect it. The only current exception is the Sasol FT fuel, whose feedstock can now be 'anything', including biomass, although originally it was made from coal at the Sasol's Secunda plant. Hydrogenated renewable jet, which is discussed in Chapter 8, has been in the approval process for several years, and appears likely to receive approval in early 2011. Other renewable jet fuels are likely several years away from approval. Similar restrictions also apply for marine fuels, which must be from a homogeneous blend of hydrocarbons derived from petroleum refining, with the exception of performance additives. Marine fuels must "be free from bio-derived materials other than 'de minimis' levels of FAME."

Because of the requirement that the biomass based jet fuel have properties nearly identical to petroleum based jet fuel; it can be handled in the current distribution system from the refinery to the aircraft.

6.3 Technology Limitations and Commercialization Gaps for Gasification

6.3.1 *Feedstock Limitations*

Thermochemical gasification processes can use a much wider spectrum of feedstocks than biochemical processes, and in that sense are less limited. Depending on the feedstock source, however, considerable pretreatment may be needed to ensure the raw material is suitable for and consistent enough for processing. Additionally, some of the feedstocks that could be used for gasification, such as coal or petroleum coke are nonrenewable and would provide limited to no environmental benefits in comparison with more traditional petroleum processes.

The specific nature of the feedstock determines the preparation steps and the means of introducing the feedstock into the reactor. Some form of size reduction is normally employed to facilitate handling and to promote more efficient reaction in the gasifier. Drying of the feedstock may also be required. If there is a dedicated feedstock source from a single site then the pretreatment steps can be well defined and the processing units can probably be operated with high efficiency. If there are multiple feedstocks which have to be handled, such as from MSW,

then the pretreatment is much more extensive. First the components, such as metal and glass, which cannot be gasified, need to be separated. Generally, there will be upstream separation of certain plastics and paper to recover recyclable material and possible upstream sorting to remove organics having high water content. Materials which are known to produce toxic compounds in the gasification reaction, such as polyvinylchloride, may also have to be removed upstream (Hackett et al. 2004). The plastics in MSW are the second-largest component and contain some 30% of the chemical energy and currently they can only be converted by thermochemical processes. In the case of jet fuel, given its tighter specifications, it may be more sensitive to feedstock inhomogeneity than other F-T diesel fuels.

6.3.2 *Production Limitations*

The technical challenges for thermochemical production encompass a wide range of system components: gasification systems, syngas cleanup systems, catalytic synthesis systems and biochemical syngas fermentation systems. Research and development has previously been conducted on several of these issues (all except biochemical syngas fermentation) for a wide variety of biomass and liquids applications. Therefore, there is a good chance that several of these issues can be at least marginally improved, although thermochemical systems seem less likely than biochemical processes to experience a game-changing technical breakthrough. This subsection examines some of the technical limitations for the processes for production of different liquid fuels from thermochemical processes.

6.3.2.1 Gasification Processes for Fischer-Tropsch Diesel Production

FT technology is not a particularly new concept, and the basic components are well established. Recent efforts have been made to integrate the gasification and FT production together and to truly focus on ways to improve the process specifically for different feedstocks. Breakthroughs are particularly desired in the FT conversion section of the plant, although it should be noted that FT breakthroughs may also be applicable to coal and petroleum coke projects. Having policies that promote synthesis routes for these types of fuels will therefore be necessary to future commercialization.

Major limitations to commercialization for biomass to FT liquids include the following:

- **Economies of Scale:** Biomass to FT units are constrained by the scale of biomass feedstock availability. The higher BTU content of coal and coke, along with the large-scale availability of these feedstocks, allows FT units based on these inputs to be built larger and more economically. The U.S. DOE estimates that commercial scale biomass to FT units will be roughly one-tenth the size (5,000 barrels per day, as opposed to a 50,000 barrel per day coal unit) based on a biomass collection radius of up to 50 miles.
- **Biomass Quality:** Building a large biomass to FT plant requires obtaining feedstock from different sources, each of which may vary in size and composition. This variation can cause gasification problems and require significant pre-processing, adding to the overall system costs. Having as consistent a feedstock as possible or a flexible gasification system would be beneficial in this regard.

- **Scale-Up:** As with most developing technologies, issues tend to arise that are not accounted for when moving from the demonstration or pilot scale to commercial operation. A measured development process is needed to allow for a gradual scale-up process.
- **Impurities and Gas Cleaning:** Due to the specific requirements of current FT catalysts, syngas must be cleaned to very tight specifications. The most pressing issues are tar removal and clean-up temperatures. Many tar removal technologies are either ineffective or very detrimental to process efficiency. Improvements in this area or selection of gasifiers that destroy tar and are economic on biomass would be beneficial. Many gas clean-up processes require cooling the syngas from gasifier exit temperatures to near 100°F before reheating the syngas back to 500°F for feed to the FT unit. Developing gas cleaning processes that can occur at elevated temperatures would improve the overall process efficiency. Efforts are being made in this area at a research level now to improve the synthesis of fuels and chemicals from biomass and coal gasification.
- **Process Specific Reactors:** Most FT reactor focus has been on large-scale coal and natural gas based systems. Because of this, many vendors do not have offerings at the scale needed for biomass and have not spent time and effort developing an optimized reactor for this smaller system.
- **Catalyst Shortfalls:** Most improvements in FT catalysts in the last 80 years have been largely incremental. Interest had been low in improving FT systems due to low priced crude oil, but recent market spikes and government initiatives have provided new research interests. Catalysts with higher per pass conversion, better selectivity, and lower sensitivity to impurities are needed to improve overall process economics. As with the reactor discussion, most of the research has been on coal-based syngas. Developing catalysts better optimized for biomass could improve the overall unit design.

6.3.2.2 Gasification Processes for Biomass to DME or MTG Production

The major issues identified with regards to development of biomass to FT projects are largely applicable to biomass to DME or MTG projects. These include the economics relative to fossil fuels, quantity of biomass needed, gas impurities/cleaning required, and lack of process maturity on biomass. The major difference between the two routes is the quality of the products. The products from the MTG process are generally much narrower in range and higher in quality than FT, so MTG fuels can be more readily integrated into the existing fuels infrastructure. A recent National Academy of Sciences study compared the FT and MTG routes for the production of transportation fuels and found, in general, that MTG was slightly more efficient and can produce fuels at a lower cost. It should be noted, however, that this study was centered on large fossil fuel based plants, so project specific economics for biomass projects need to be considered. DME, on the other hand, is a gaseous fuel that would likely be limited to niche applications.

Many of the technical limitations for biomass-based DME or MTG processes are related to having a design focus that is centered on biomass. Most gasification-based projects are designed very large and use fossil fuels as the basis. Market analysis would be needed to find the niches where biomass based gasification routes could be successful. Developing designs that fit these niches will be important to future commercial efforts. This would include locations with tipping fees for wastes and co-firing of biomass with fossil fuels. In addition, locations with few other

options for local fuel generation and/or strong policy drivers in the renewable sector provide additional project incentives. These are two reasons why China and Sweden are market leaders in DME projects.

Biomass-to-MTG facilities may be better suited for small-scale, distributed use than other gasification based routes, since the raw product can be used in the existing fuels infrastructure with a limited amount of product treatment. The ability of this equipment to be economically utilized in this sort of application must be demonstrated. Proving that equipment is robust and effective for modular application may be a more suitable market approach that trying to compete with large-scale fossil based designs.

While DME production development has occurred in Asia and Europe, the feasibility and cost of utilizing the fuel in California would need to be investigated in more depth before a biomass-to-DME route is considered for commercial development. Improvements in the one-step DME design would likely improve the economics of the process and enhance the chances of greater acceptance as a transport fuel if the integration issues can be overcome. When developing biomass to DME process technology, process innovation should be considered to allow for the flexibility of producing either DME or gasoline/olefins. The process should be tunable to adapt to market demands. While this will potentially increase the capital cost of a biomass to DME unit, the potential cash flow may be improved through better long-term product prices.

6.3.2.3 Gasification Processes for Ethanol Production

The technical limitations for thermochemical processes for ethanol production are similar to those discussed above for the other processes. They include the following:

- **Scale issues for gasification/alcohol synthesis methods:** Economies of scale tend to favor large systems, which would require biomass feedstock inputs of more than 1000 tons per day. However, biomass gasification systems at these scales have not been reliably demonstrated. For widespread implementation of thermochemical processes, it is likely that a system must be developed that can be economical at scales of less than 1000 tons per day.
- **The presence of tars in biomass-derived syngas:** Most existing biomass gasification systems (e.g., fluidized or fixed bed gasifiers) produce a syngas that contains significant quantities of condensable hydrocarbons (i.e., “tars”) that must be removed or destroyed prior to downstream processing, where these constituents can plug equipment and/or poison catalysts. To achieve this, one of two technologies must emerge: (1) biomass gasification systems that yield a syngas with minimal tars, or (2) an efficient, low-cost catalytic process to “crack” or “reform” the tars into lighter hydrocarbons.
- **Lack of syngas fermentation technologies:** While syngas fermentation technologies like those being developed by Coskata and INEOS Bioenergy offer promise to avoid issues of scale that may hinder FT technologies, these biological systems have yet to be demonstrated on a scale approaching those of commercial facilities.

- **Lack of overall process integration:** Like biochemical pathways, there are a number of potential system components that may be used to configure thermochemical cellulosic ethanol systems. The specific subsystems selected by the leading developers may not yield the optimal thermochemical system. Therefore, this issue should be investigated to evaluate the multiple options.
- **Catalyst yield and selectivity issues:** There is no catalyst today that can produce a high level of fuel grade ethanol from syngas. Problems include low per pass conversion and/or production of a range of byproduct alcohols or other chemicals. Improvements in catalyst performance will help the economics of units that depend on this technology.

6.3.2.4 Gasification Processes for Jet Fuel Production

The production limitations for jet fuel are similar to those for gasification followed by Fischer-Tropsch processing. The technologies are relatively mature and are used at commercial scales in other parts of the world where economics are more favorable. In the US, however, the high production costs associated has been the major limitation that has prevented significant commercial development.

6.3.3 *Infrastructure, Distribution, and Utilization Limitations*

An important issue with biomass to liquid fuels is that the final product fuels must meet the requirements for more traditional transportation fuels. These issues are specific to the particular type of fuel being produced.

Fischer-Tropsch diesel, with the addition of a lubricity additive, is a high quality diesel fuel with a high cetane number and good flow properties. This fuel should be completely compatible with existing fueling infrastructure, and is already used as a blending stock in some real applications. Similarly, synthetic gasolines should also be compatible with the existing infrastructure, provided they can meet the applicable fuel standards. In fact, MTG units tend to produce a relatively narrow product stream, so such projects would not require nearly the integration into the petroleum refining infrastructure as pyrolysis or FT units. Even with only a limited amount of raw product treating, the gasoline is very compatible with the existing fuels infrastructure and local use.

DME has significant limitations from a utilization standpoint. DME is a gaseous product that currently does not have established routes for usage and distribution. DME would require a fueling and distribution infrastructure similar to that of LPG. As such, it would require specialized refueling systems. It would also require specially modified vehicles due to its low lubricity and viscosity and corrosiveness that have currently only been developed in limited numbers and on a demonstration basis. DME also has a lower energy content than petroleum diesel. Due to these reasons, DME would likely only be applicable for niche applications.

Methanol can be used in either internal combustion engines or in fuel cells. This section focuses on the use of methanol in internal combustion engines. The use of methanol in fuel cells is

discussed later in section 11.2.3, which discusses fuel cells fueled by both hydrogen and methanol.

Methanol has characteristics similar to ethanol, in that it would require special vehicles and it cannot be transported via pipeline. The use of methanol in conventional vehicles or in specially designed vehicles is considerably less developed than for ethanol, as discussed in section 6.2.3. Methanol also has a lower energy density than ethanol, and has only about 51% of the BTU content of gasoline by volume. Methanol is also even more corrosive than ethanol. Additionally, unlike ethanol, which has been approved at levels of 10-15% in conventional gasoline, the use of low blends levels of methanol is not permitted in the US. The European Fuel Quality Directive does, however, allow up to 3% methanol to be blended into gasoline. It is reported that methanol is being used as a low level blend agent in the United Kingdom. This is a blend of methanol and ethanol, in addition to co-solvents and other additives, to ensure compliance with vapor pressure and fuel stability criteria.

Similar to ethanol, the use of higher levels of methanol in vehicles requires the development of specialized FFVs. Some of the adjustments that are needed for methanol FFVs are similar to those needed for ethanol FFVs, as discussed in section 3.2.3.1. These include alcohol sensors to monitor the fuel mixture and adjust the fuel flow and timing, larger fuel injectors, a larger fuel tank, a stainless steel fuel system, and other features for cold starts. The methanol industry suggests that these changes add an incremental cost of only \$50-\$150 per vehicle or less (Dolan, 2008; Lynn, 2009). On the other hand, with the decline in interest in methanol, no methanol FFVs have been produced in the US since 1999, which represents a significant limitation on the potential use of methanol in the fleet.

It is worth considering the use of methanol in existing FFVs. In this regard, it must be noted that automakers most certainly object to this application since current E85 FFVs are not designed for use with M85. Material compatibility issues, especially over the long term, would be a major issue. Evaporative emissions would likely also increase due to increased permeability. Fuel injector capacity would also probably be an issue, given the differences in energy density between ethanol and methanol. Thus, methanol would have to be limited to lower levels, such as M67.5 or E42.5M28.5G29, to achieve the same air-fuel ratio as for E85. Given the limitations with potential use of methanol in E85 FFVs and California's relatively stringent requirements on bringing new fuels into the marketplace, it appears unlikely that such an application would be practical for fleetwide use in the foreseeable future. It is possible that this question could be considered from a more research standpoint as part of the upcoming mixed alcohol program (Durbin et al., 2010).

Ethanol would be limited by its pipeline and vehicle incompatibilities, and lack of dedicated fuel pumps for higher ethanol blends levels. The significance of these limitations is discussed in greater detail in chapter 3.

6.4 Environmental and Other Considerations

For thermochemical systems, one important environmental consideration is the emissions that might be generated during the production process. This has been a particularly important issue for processes using mixed waste feedstocks or MSW. Prior to 2005, information in this area was

more limited. University of California at Riverside researchers conducted a limited study in 2005 of three prototype thermochemical conversion technologies (Durbin and Welch, 2005). Since then, significant efforts have been made to develop and analyze independent emissions data from thermochemical processes worldwide. These data are developed from independent source test reports, compliance reports from regulatory agencies, and peer-reviewed publications. In a more recent study, University of California researchers evaluated a more comprehensive dataset of such independent emissions data from thermochemical processes (University of California, Riverside, 2009). Results from this analysis indicated that pyrolysis and gasification facilities currently operating throughout the world with waste feedstocks meet each of their respective air quality emission limits. With few exceptions, most processes meet all of the current emission limits mandated in California, the United States, the European Union, and Japan. For toxic air contaminants (dioxins/furans and mercury), every process evaluated met the most stringent emission standards worldwide. Facilities with advanced environmental controls were found to be very likely to meet regulatory requirements in California. The actual impacts of specific facilities will need to be evaluated on a case-by-case basis as part of a local permitting process.

For the lifecycle GHG analyses, CARB has yet to conduct any analyses on gasification processes to evaluate the carbon intensity values for these processes for the LCFS. As thermochemical gasification derived fuels begin to be used to meet the LCFS requirements, such analyses will need to be performed. For renewable jet biofuels, the Commercial Aviation Alternative Fuel Initiative environmental team is working on a lifecycle emissions framework.

Fischer-Tropsch fuels may also provide some benefits in tailpipe emissions compared to traditional diesel, as FT fuels generally have more favorable emissions characteristics, such as lower aromatics and density. The emissions differences for jet fuels would probably be less, since jet fuel is made to tighter specifications.

6.5 On-going Research

The discussion above deals predominantly with the traditional methods of gasifying coal or petroleum coke using high temperatures, high pressures and steam/oxygen for the gasification or a lower temperature and pressure and a circulating hot solid to convert the steam/coal (biomass) to a gaseous mixture. Some of the other gasification methodologies include hydrogasification or steam hydrogasification. These processes carry out gasification using hydrogen or a combination of hydrogen and steam/water in place of oxygen. Hydrogasification has been used at some level since the 1930s for synthetic natural gas. The hydrogen for the reaction can be supplied internally through either a water gas reaction of the char or by steam methane reforming of the product synthesis gas. While hydrogasification does not require the use of oxygen, which can be expensive to produce, it does require high pressures (~100 atm) or a catalyst to carry out the reaction. Additionally, the reaction is considerably slower than oxygen-driven gasification. A combination of these factors has led to a lack of commercial success or interest.

Steam hydrogasification uses a Steam Hydrogasification Reactor (SHR) as the first step for production of syngas. The process inputs are a wet biomass slurry combined with water and hydrogen and it has been developed by Norbeck, et al. (2008). The SHR temperature is typically 700 to 800°C with initial hydrogen pressures around 100 psi and the output gas is composed of

primarily CH₄, CO, CO₂, H₂ and steam. Following gas cleanup, the primary gases are fed into a Steam Methane Reformer (SMR) reactor to generate the syngas. The excess H₂ in the syngas is separated and recycled to the SHR and the syngas is processed in a Fischer-Tropsch Reactor (FTR) to produce the desired product. A key advantage of this process is that smaller units can be economical because neither oxygen, which is very expensive, nor air, which significantly decreases the calorific value of the product gases because of the high nitrogen content, are required in the gasification reaction. The process also utilizes a wet feedstock, so there is no need for pretreatment to dry the feedstock. Other advantages of this process are the ability to generate a syngas with a flexible H₂/CO ratio, the low production of tar in the process, and the low pressures and temperatures used by the process in comparison with other gasification processes. One disadvantage of this process is that it is still slower than gasification processes that utilize oxygen, although it is much faster than hydrogasification. This process also has only been demonstrated at a lab scale so there is considerable research needed to prove the viability of this technique at a commercial scale.

6.6 Recommendations for Gasification Related Fuel Technologies Research

Gasification offers the potential to utilize a wider range of feedstocks than other biomass conversion processes. There are currently a number of challenges that must be overcome to make gasification economically viable for biomass, however. The areas of need/issues for gasification research are similar for the different processes to produce different fuel products. One of the main issues is the economy of scale. Since gasification is a relatively complex process, larger facilities tend to be more economic. For biomass, however, the scale of the gasification unit will be limited by the availability of biomass, which is generally limited to a collection radius of up to 50 miles. The U.S. DOE estimates that commercial scale biomass to FT units will be roughly one-tenth the size of those for a coal-based unit (5,000 barrels per day, as opposed to a 50,000 barrel per day coal unit). The ability to develop biomass gasification units at the smaller scales that might be needed to effectively and economically process biomass will be critical. Some specific market conditions could be helpful in making these types of projects economic. The best opportunities may come in the following areas:

- **Tipping Fees for Biomass:** Having low or negatively priced feedstock would be helpful to make biomass FT projects attractive. This may be a main driving factor behind the Rentech Rialto project. Biomass at this price would only likely be present near large population centers without ample land for waste disposal and policy drivers pushing for waste reduction.
- **Refinery Integration/Off-Take:** The upgrading and processing of FT products to finished transportation fuels can add considerable cost to a stand-alone facility. Integrating the project with an established refiner may reduce this capital and operating cost requirement.
- **Co-firing of Biomass:** Combining biomass with coal or petcoke will reduce the environmental impact relative to straight fossil fuel feedstocks while taking advantage of the economy of scale that would come with a fossil based facility.

Taking these three factors into account, it appears that locating a biomass gasification to liquid fuels facility near a large metropolitan area and using urban wood wastes could be the most economic arrangement for such a facility.

Neither biomass gasification nor the use of FT, DME, or MTG technology is a particularly new concept. The basic components for each are well established. Recent efforts have been made to integrate gasification and FT together and truly focus on ways to improve the process specifically for biomass feedstocks. Breakthroughs are particularly desired in the FT conversion section of the plant, although it should be noted that FT breakthroughs may also be applicable to coal and petroleum coke projects.

Most FT reactors have been made for large-scale coal and natural gas based systems. Because of this, many vendors do not have offerings at the scale needed for biomass and have not spent time and effort developing an optimized reactor for this smaller system. Developing catalysts with higher per pass conversion, better selectivity, and lower sensitivity to impurities would improve the overall process economics. As with the reactor discussion, most of the research has been on coal-based syngas; developing catalysts better optimized for biomass could improve the overall unit design.

There are also issues with the specific processing requirements for biomass feedstocks. Biomass tends to be more inhomogeneous compared to other potential fuel sources, such as coal. Building a large biomass to FT plant will require obtaining feedstocks from different sources, each of which may vary in size and composition. This variation can cause gasification problems and require significant pre-processing, adding to the overall system costs. Having as consistent a feedstock as possible or a flexible gasification system would be beneficial.

The clean-up of the syngas is also important since the FT and other such catalysts must be cleaned to very tight specifications. The most pressing issues are tar removal and clean-up temperatures. Many tar removal technologies are either ineffective or very detrimental to process efficiency. Many gas clean-up processes require cooling the syngas from gasifiers exit temperatures to near 100 °F before reheating the syngas back to 500 °F for feed to the FT unit. Developing gas cleaning processes that can occur at elevated temperatures would improve the overall process efficiency.

The research opportunities for different gasification pathways, such as FT diesel, FT jet fuel, or methanol-to-gasoline (MTG), tend to be similar. These include catalyst improvements, gas clean-up, and integration or consolidation of process steps. These main ideas are discussed below with an initial emphasis on FT diesel. Some of the more novel research areas that have been initiated (and which deserve consideration for further research support by PIER) include:

- **Economies of Scale:** There is a need to develop much smaller gasification/FT units that can be operated economically, since the available biomass within a reasonable transportation distance cannot support the large units designed for natural gas or coal.
- **Scale up:** Demonstration and pilot scale units need to be developed to explore issues which may arise when designing and operating a commercial size unit. Additionally, issues tend to arise that are not accounted for when moving from the demonstration or pilot scale to

commercial operation. A measured development process should occur that performs the scale-up gradually.

- **Biomass Quality:** Pretreatment processing of the biomass prior to gasification may be an option for producing a more uniform product for the gasifier. The impact of pretreatment of biomass feedstocks on the subsequent gasification processing could be evaluated.
- **Selective FT Catalyst:** There is a need to develop FT catalysts with higher per pass conversion, lower sensitivity to impurities and/or process conditions, and better selectivity for carbon number, which dictates the type of products produced (the split between gasoline, jet, and diesel boiling range compounds). Meeting these objectives would require the successful manipulation of the FT chain-growth mechanism. Unfortunately, to date, none of the proposed (and hotly contested) FT mechanisms have indicated how this goal could be achieved. Monolithic and edge coated FT catalysts are being investigated for selective FT synthesis.
- **FT Process Intensification:** Process intensification is the consolidation of multiple process steps into a fewer number of units. This helps to improve efficiency and lower overall costs. Options include development of economic reactor technologies for syngas conversion based on process intensification, catalyst/reactor integration, and heat management to improve the viability of biomass-based FT systems. Development of modular-type reactor systems could help improve the viability of distributed biomass gasification plants.
- **High Temperature CO₂ and Sulfur Removal:** Syngas produced from biomass conversion includes a large fraction of CO₂ and may include some amount of sulfur. The presence of CO₂ can have detrimental effects on syngas conversion, and even small amounts of sulfur can be poisonous to FT catalysts. To maintain the H₂/CO ratio at about 2.1:1, CO₂ has to be removed from the recycle loop. High temperature CO₂ removal using advanced sorbents or membranes could improve the process efficiency by reducing the cooling and reheating requirements. High temperature sulfur removal has been demonstrated using circulating beds of solid sorbents. None of these technologies are commercially available. A CaO/CaCO₃ looping process to capture/separate process CO₂, which operates at high temperature, has been developed, but only at a demonstration scale.
- **Catalytic Biomass Gasification:** In addition to traditional noncatalytic gasification processes, catalytic gasification of biomass can be used to lower the operating temperature, making the process more economically feasible. Typically, temperatures above roughly 750°C are required for noncatalytic gasification. Gasification catalysts can lower the operating temperature to around 600°C, resulting in substantial energy savings. However, rapid deactivation by tar formation at the lower temperatures of catalytic gasification has led to the search for more tar-resistant, but still active, gasification catalysts.

The importance of developing smaller scale units for biomass gasification suggests that other technologies may also need to be developed. Steam hydrogasification combines a steam hydrogasification reactor (SHR) with a Steam Methane Reformer (SMR) to produce a syngas for Fischer-Tropsch processing. Since the process does not require oxygen, which is very expensive, or air, which significantly decreases the calorific value of the product gases because of the high nitrogen content, SHR may be more economical to produce at a smaller scale. Also, because SHR uses a wet feedstock, there is no need for pretreatment to dry the feedstock.

7 Pyrolysis

7.1 Introduction

Pyrolysis is another thermochemical process that can be used to convert biomass to a liquid fuel. Pyrolysis differs from other thermochemical processes in that it is done in the absence of oxygen and at lower temperatures. The resulting pyrolysis oil is also a fairly low quality product that requires more significant upgrading to meet transportation fuel quality specifications. In this chapter, the technical development and ongoing research for pyrolysis as a transportation fuel are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for pyrolysis are provided.

7.2 Development of Pyrolysis for Transportation Fuels

7.2.1 *Pyrolysis Feedstocks*

The feedstocks applicable for pyrolysis are similar to those that can be used for gasification, as discussed in chapter 2 and 6.2. This includes most carbon containing materials, such as raw or processed biomass, as well as coal and other similar materials. As with gasification, biomass feedstocks are generally the most challenging to process since they are less homogeneous and can have higher levels of impurities.

The pretreatment steps for pyrolysis are essentially the same as for gasification, as discussed in 6.3.1. The pyrolysis process is somewhat more forgiving than gasification for processing mixed waste products. Therefore, pyrolysis reactors are sometimes used to generate the feed for gasification reactors.

7.2.2 *Pyrolysis Production*

7.2.2.1 Production Technology

Pyrolysis oils are produced through heating biomass feedstocks in the absence of oxygen to moderate temperatures (600 to 1000 °F). This process produces three distinct phases of material in the pyrolysis reactor: a gas phase (10 to 20 percent) consisting of light hydrocarbons and volatiles, a liquid, bio-oil phase (60 to 70 percent), and a solid char (10 to 20 percent). The bio-oil is a mixture of a wide range of chemicals including paraffins, naphthenes, aromatics, phenols, acids, and asphaltenes, along with roughly 25 percent water.

The main technology employed today in the production of pyrolysis oil is fast pyrolysis. Fast pyrolysis occurs at a 950°F under atmospheric pressure with a residence time of 2 seconds or less. Fast pyrolysis can take place in a fluidized bed reactor without the need for water or a catalyst. Both circulating and bubbling fluidized beds have been developed for pyrolysis oil production. In these reactors, an inert sand is typically used as the heat carrier. A schematic for a circulating fluidized bed can be seen in Figure 7-1. Other reactor types sometimes used include rotating cone pyrolyzers and vacuum units.

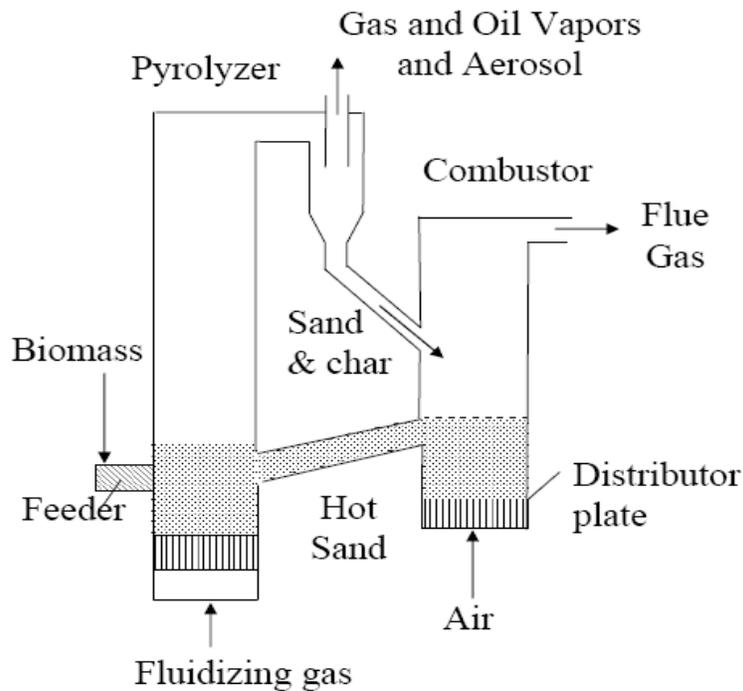


Figure 7-1: Circulating Fluidized Bed Schematic, Pyrolysis Oils.

Pyrolysis oils have a variety of utilization options including producing electricity, manufacturing chemicals, or being converted into fungible transportation fuels. Without any significant upgrading, the oils themselves are of low quality due to high levels of water, oxygen, and acids. In addition, raw pyrolysis oils are very viscous, degrade quickly, have large amounts of particulate matter, and are very sensitive to changes in temperature. By removing water and stabilizing the oil for pumpability and minimum storage needs, the oil can be burned directly in specialized fuel oil burners or combustion turbines. Much more extensive upgrading is necessary to convert the pyrolysis oil into components that can be used as a transportation fuel.

Technologies typically utilized in the petroleum refining industry have been adopted to upgrade bio-oils to transportation quality fuels. Hydrotreating catalysts can convert raw bio-oils, in the presence of hydrogen, to diesel, jet fuel, or gasoline quality material. Catalytic cracking units can also be used on bio-oil to produce material close in composition to gasoline. In each of these units, the yield and quality of the finished product varies based on the quality of the raw bio-oil and the type of catalyst used. Data from UOP and Pacific Northwest National Laboratory shows that roughly 25 to 40% gasoline or diesel boiling range product will be produced in a typical pyrolysis oil hydrocracker or catalytic cracker, with the majority of the remaining products being water and CO₂. The high level of oxygen present in the raw pyrolysis oil is largely removed from the oil in the finished product, greatly reducing the yield of fungible fuel. Improvements in upgrading catalyst have enhanced the quality of the fuels produced through bio-oil catalytic upgrading. Historically, the quality of the gasoline and diesel cuts were low and required blending with higher quality materials to produce on-road fuels. Recent work by UOP has produced hydrogenated fuels from bio-oils near on-road quality. There has not, however, been extensive testing performed on neat blends of on-road fuels from bio-oils due to on-going quality issues and lack of an agreed quality standard.

Other approaches have been taken for upgrading bio-oils to transportation fuels. The first is the use of microwaves. The use of microwave technology for upgrading pyrolysis oils was first experimented with in the 1970s. Demonstration projects are on-going at the university level, most notably the Norwegian University of Life Sciences and the University of Minnesota. Despite these efforts, the extent of microwave investigations appears limited compared to most of the other methods, so new developments in this front could be a significant upgrade over the current technology being used. The second is the use of catalysts within the pyrolysis reactor to convert the vapors to higher quality fuels prior to quenching to the liquid phase. This route suffers from catalyst deactivation issues and the need to use precious metal catalysts. Most of the investigations into these two upgrading routes are going on only at the academic level. Gasification of pyrolysis oils to synthesis gas (syngas) with subsequent conversion to fuels or chemicals over a variety of different catalyst types is also an option. This route will be covered in the chapter on thermochemical conversion.

7.2.2.2 Commercial Development

The development of a platform to commercialize pyrolysis oil technology is not a new concept. Efforts have been underway since the 1980s to develop technologies that can meet a commercial need. Commercialization of pyrolysis initially appeared to have an advantage over other cellulosic biofuel production routes in the 1990s and earlier this decade, but it appears that the difficulty in using and marketing the pyrolysis oil has now led to the technology falling behind. While there have been limited niche successes, there has been no widespread commercialisation as of yet. There are four companies that appear to be most heavily engaged in commercialization efforts today: Dynamotive, Ensyn/UOP/Envergent, BTG, and PyTec. Comments on their history, facilities, and applications are outlined below:

- **Dynamotive:** In development since the early 1990s, Dynamotive is a Canadian firm that is currently operating two commercial pyrolysis units. The oil produced is used largely in boilers for power and heat. The abundance of inexpensive feedstock and high heating demand in Canada is a main reason for these applications. The focus historically has not been on upgrading the bio-oil to transportation fuels; recent work performed by Dynamotive has demonstrated that two stage upgrading is possible on its bio-oil, although no definitive plan for commercial development has been outlined.
- **Ensyn:** Another Canadian company, Ensyn began work in pyrolysis in 1980 with development of their specific pyrolyzer in 1984. As with Dynamotive, their technology has typically been focused on use of pyrolysis oil for power or heat applications. In March 2009, Ensyn announced a partnership with UOP to create Envergent; the company plans on using Ensyn's rapid thermal pyrolysis experience and UOP's catalytic upgrading knowledge to develop green gasoline and diesel from pyrolysis oil. Envergent has set a goal of 2012 for its first commercial pyrolysis oil to transportation fuel unit.
- **BTG:** Beginning pyrolysis development in the early 1990s, this Dutch firm has an operating 50 tpa plant in Malaysia for the production of power. They have recently started a company focused solely on the use of their rotating cone pyrolysis

technology to make oils from biomass (BTG BTL). It appears that most of their focus is on utilization of bio-oils for power, although studies have been performed in Europe on upgrading of oils in existing refineries.

- **PyTec:** This German firm has an operating CHP plant in Germany using their ablative pyrolysis technology. Applications appear to be focused on CHP.

To date, Dynamotive has been the strongest, most active company, with focus on applications using pyrolysis oil in industrial turbines or boilers. With high petroleum prices, ramped up government support programs, and the partnership with UOP, it appears that Ensyn may be poised to close the gap with Dynamotive in efforts to commercialize their pyrolysis oil technology.

Two major themes are clear from the current commercial efforts for pyrolysis oil technology. The first is the use of pyrolysis oil for heat and power, not transportation fuels. Given the extensive history in pyrolysis oil development, it is clear to all the companies above what the barriers are to converting pyrolysis oil into diesel and gasoline. The fact that until the Ensyn/UOP joint venture this year, not one of the firms is currently known to be integrating upgrading technologies with their development plans may be indicative of the difficulty of the oil upgrading problem. Second, most of the companies are based in locations, or have based their plants, in areas with abundant and inexpensive feedstock. The low oil yield and oil value from pyrolysis units makes having low cost feedstock a very important factor in achieving an economically attractive project.

Besides the four companies listed above, there are a number of small organizations and research institutes that are exploring novel applications for the production of pyrolysis oils. Since no specific upgrading routes to produce fungible transportation fuels from pyrolysis oils have been commercialized, this opens the possibility that companies that can solve these issues may be able to generate intellectual property.

An approach that has been hypothesized for the commercialization of pyrolysis oils to transportation fuels is a large number of small, distributed pyrolyzers producing bio-oil at multiple locations. This oil would then be transported to a large central facility for upgrading. Since the pyrolysis reactors themselves are fairly simple pieces of equipment without significant infrastructure needs, they may adapt well to distributed deployment relative to upgrading units which will benefit more from the economy of scale seen in a large facility. Typical petroleum refinery hydroprocessing or catalytic cracking units are 10,000 barrels per day or more, while most pyrolysis oil development units being demonstrated or conceived are in the hundreds of barrels scale. Analysis by UOP shows that aggregating pyrolysis oil to a refinery scale upgrading unit would reduce the capital cost of upgrading by a factor of three for the same amount of bio-oil when compared to multiple, distributed upgrading units. Converting biomass to pyrolysis oil makes transport easier and more economic. However, the poor quality of the raw bio-oils makes storage a major concern; bio-oil would need to be contained in stainless steel to prevent corrosion and processed quickly to prevent degradation of components.

7.2.3 *Distribution and Utilization of Pyrolysis Oil*

The poor quality of the pyrolysis oil and the associated requirements for upgrading is one of the more critical issues with the development of the pyrolysis technology for transportation fuels. Pyrolysis oil quality issues include a low energy content, high oxygen content, water, and low pH. Pyrolysis oil is a mix of various chemical constituents that will vary depending on the feedstock characteristics as well as the composition of the gas in which pyrolysis takes place, the final temperature, and the rate of heating the biomass. This makes a heterogeneous mix that is not ideal from the standpoint of processing/upgrading pyrolysis oil to more pure marketable products compared with other cellulosic routes. Besides blending problems, pyrolysis oils will need to be stored in material that will not corrode due to the acidic character of the fuel.

Pyrolysis oils have a variety of utilization options including the production of electricity, the manufacture of chemicals, or conversion into fungible transportation fuels. By removing water and stabilizing the oil for pumpability and minimum storage needs, the oil can be burned directly in specialized fuel oil burners or combustion turbines. The oxygen in biooil has to be reduced via hydrotreating and hydrocracking to upgrade the pyrolysis oil to hydrocarbon fuels, which are also referred to as green gasoline and green diesel. Upgrading pyrolysis oil to high-quality hydrocarbon fuels has been demonstrated, but not at a commercial scale.

Upgrading pyrolysis oils into components that can be used for transportation fuel requires extensive processing. Biomass derived gasoline and diesel need to meet ASTM D4814 and ASTM D975, respectively, to enter the fuel market. Hydrotreating catalysts can convert raw bio-oils, in the presence of hydrogen, to diesel, jet fuel, or gasoline quality material. Data from UOP and Pacific Northwest National Laboratory shows that roughly 25 to 40% gasoline or diesel boiling range product will be produced in a typical pyrolysis oil hydrocracker or catalytic cracker, with the majority of the remaining products being water and CO₂. Historically, the quality of the gasoline and diesel cuts were low and required blending with higher quality materials to produce on-road fuels. Another approach is microwave technology that is being studied at the university level, most notably the Norwegian University of Life Sciences and the University of Minnesota. Despite these efforts, the extent of microwave investigations appears limited compared to most of the other methods, so new developments in this front could be a significant upgrade over the current technology being used. The second is the use of catalysts within the pyrolysis reactor to convert the vapors to higher quality fuels prior to quenching to the liquid phase. This route suffers from catalyst deactivation issues and the need to use precious metal catalysts. Most of the investigations into these two upgrading routes are going on only at the academic level.

Some issues of handling and storage of pyrolysis oil as a renewable source for green transportation fuels are the acidity and stability of pyrolysis oil. Biooil produced from biomass via pyrolysis processing contains organic acids with PH 2.0 – 3.7, which are corrosive to carbon steel (Ringer, et al., 2006). Biooil used as an intermediate step for green gasoline and green diesel has a certain shelf life for storage for later use. However, biooil can be stored only for weeks and at most months depending on the feedstocks of the biooil, as viscosity will gradually increase and phase separation will occur over time (Ringer et al., 2006). NREL has been investigating processes such as hydrotreating to refine the biooil to a more stable, less acidic state for transport or use as fuel. If the pyrolysis oil can be upgraded to gasoline or diesel fuel meeting transportation specifications, these fuels could be distributed using existing gasoline and

diesel pipelines and storage tanks and dispensed via current retail station infrastructure without any modification.

Another product of pyrolysis production is biochar. This is a solid charcoal-like substance that has a high carbon content. The amount of biochar produced in pyrolysis is a function of the reaction conditions, with more biochar produced at lower temperatures. Biochar can be used as a soil amendment and as a potential method for carbon sequestration (International Biochar Initiative, 2010). Biochar acts as a carbon sink since CO₂ is released when plants, trees and other vegetation dies and decompose or burn. If the plant is processed via pyrolysis instead of being allowed to decay, the biochar can be put into the ground in a much more stable form, such that it will not be as readily released to the atmosphere. When used as a soil amendment, or in conjunction with organic and inorganic fertilizers, biochar can significantly improve soil tilth, productivity, and nutrient retention and availability to plants. In the soil, biochar provides a habitat for soil organisms and most of the applied biochar can remain in the soil for several hundreds to thousands of years. Biochar can help reverse soil degradation and facilitate sustainable food and fuel production in areas with severely depleted soils, scarce organic resources, and inadequate water and chemical fertilizer supplies. The effectiveness of biochar as a soil amendment is dependent on the properties of the biochar and the characteristics of the area it is being applied to, including soil type, condition, temperature, and humidity. Biochar is most effective for plants that grow under high potash and elevated pH conditions (Lehmann et al., 2003). Research is still needed to determine the agronomic value of different types of biochar produced by different feedstocks and pyrolysis technologies and to determine the net carbon sequestration and longevity of the sequestration.

7.3 Technical Limitations and Commercialization Gaps for Pyrolysis

7.3.1 Feedstock Limitations

Similar to gasification, pyrolysis processes can use a much wider spectrum of feedstocks than biochemical processes. Important considerations for feedstocks include the need and extent of the preprocessing needed for the feedstock and if it is nonrenewable, such as coal.

7.3.2 Production Limitations

The main technical and commercialization limitations are the size scaling of the pyrolysis processing plants and the fact that the pyrolysis oil produced is a low quality product. These limitations are summarized below:

- **Pyrolysis Oil Quality:** The quality of raw pyrolysis oil is very poor, requiring extensive upgrading before it can be used as an on-road transportation fuel. While technologies exist to do this, the high cost and low yield have typically made conventional options too expensive.
- **Lack of Integration with Petroleum Refiners:** The most logical route for upgrading bio-oils would be partnership with petroleum refiners. Blending to specifications is not enough; refineries and engine manufacturers will want to perform extensive testing before authorizing any transportation fuels using either pyrolysis oil in direct blending or

as a process feedstock. The high acid and oxygen content of the pyrolysis oils will limit the interest and ability of many refiners to accept pyrolysis oil without extensive pre-treatment.

The lack of interest from oil companies for pyrolysis oil technologies should not be perceived as a general lack of interest in biofuels. Oil companies have announced major partnerships and investments in the production of biofuels from other routes such as BP (with Verenum), Shell (previously in a partnership with Choren, now dissolved), and ExxonMobil (with Synthetic Genomics). Given the strong interest that oil companies have in staying engaged in transportation fuel production, this technology choice can be perceived as their belief in what is the best route to produce advanced biofuels.

- **Small Sizes:** A large-scale pyrolysis oil plant of 100,000 tons (roughly 2200 barrels per day) is equivalent to 0.5 to 2% of the input to a typical crude oil refinery. Refiners will likely be reluctant to make major changes to their process to accommodate such a small amount of feedstock. In addition, new refinery applications (such as hydrocracking and hydrotreating) are typically built in the 10,000 barrel per day range or higher due to economies of scale. This means that it is unlikely that a separate upgrading unit would be present at the pyrolysis oil unit, and would require a central upgrading facility to be economic.

7.3.3 *Pyrolysis Oil Upgrading for Distribution and Utilization*

The main issue with utilizing pyrolysis oil produced via the pyrolysis process is the poor quality oil that requires considerable upgrading to meet transportation specifications. The pyrolysis oil produced varies in oxygen content and viscosity according to the feedstock used. Hydrotreating and hydrocracking can be used to upgrade the pyrolysis oil to a hydrocarbon fuel. Although hydrotreating and hydrocracking are commercial processes, upgrading pyrolysis oil to transportation-quality hydrocarbon fuels has not been demonstrated at a commercial scale. Research is being conducted in more advanced techniques, such as microwave technology, but this work is being conducted on an academic level. The acidity and stability of pyrolysis oils is an issue for storage and handling, although pyrolysis oils would essentially be an intermediate step for use as a transportation fuel.

7.4 **Environmental and Other Considerations**

The environmental issues associated with pyrolysis processes would be similar to those discussed for thermochemical gasification processes. Based on the evaluations by the University of California at Riverside researchers (Durbin and Welch, 2005; University of California Riverside, 2009) it appears that pyrolysis production facilities with advanced environmental controls should be able to meet regulatory requirements in California. Similar to gasification processes, CARB has not conducted an evaluation of the carbon intensity values for pyrolysis-derived fuels being used to meet the LCFS requirements. Such analyses would need to be performed if such fuels begin to enter the California marketplace.

7.5 Ongoing research

There is considerable ongoing research in the area of pyrolysis and pyrolysis systems. Table 7-1 provides a listing of the groups conducting research in pyrolysis and the major area of their research.

Table 7-1: U. S. Labs working on Various Aspects of Pyrolysis oils

Laboratory	Major Area
Pacific Northwest National Laboratory (DOE)	Fluidized-bed pyrolysis Catalytic pyrolysis Technoeconomic assessments Improved catalysts for bio-oil hydrogenation Small batch testing of model compounds,
National Renewable Energy Laboratory (DOE)	Bio-oil neutralization and stabilization Catalytic Pyrolysis Mild-hydrotreating batch reactor Technoeconomic assessments Hot-gas filtration
Eastern Regional Research Center (USDA-ARS)	Pyro-probe GCMS Bubbling fluidized-bed fast pyrolysis Catalytic pyrolysis
Iowa State University	Fast pyrolysis research Interdisciplinary studies Bio-oil stabilization
University of Massachusetts-Amherst	Catalytic fast pyrolysis Upgrading of bio-oil by aqueous-phase processing Bio-oil stabilization Fundamental kinetic model of pyrolysis
University of Maine	Fluidized-bed fast pyrolysis Catalytic upgrading of bio-oil
Washington State University-Pullman and Tri-Cities	Pullman Campus Fundamental studies of reactions Tri-Cities Campus Comparisons of microwave heating and bubbling fluidized-bed
Mississippi State University	Extensive review of fast pyrolysis Auger pyrolysis unit Bio-oil hydrotreating
Virginia Tech	Fluidized-bed pyrolysis Chicken litter pyrolysis Fractional catalytic pyrolysis Bio-oil stabilization
University of Minnesota	Microwave-assisted pyrolysis Catalytic pyrolysis to produce stable bio-oil Reach and maintain exothermic reactions Low-cost distributed system for on-farm application
University of Georgia	Slow pyrolysis and Intermediate pyrolysis

7.6 Recommendations for Research for Pyrolysis for Transportation Fuel

There are still many technical limitations to the development of biomass pyrolysis into a viable source for transportation fuels. The cost and potential economic return of pyrolysis oil facilities do not appear to be superior to other second generation biofuels facilities, thus they will require higher oil prices or incentives to reach suitable economic returns. Pyrolysis can use a range of different feedstocks, although the quality of the bio-oil end product will vary to a greater degree when compared to a gasification route. This can be an issue depending on how the oil is used or upgraded.

To become commercial, pyrolysis oil routes will need to achieve technical advancements and find a specific geographic niche for the technology. One application where pyrolysis could potentially be deployed is using medium scale conversion systems (e.g., 50 to 250 tons/day) in a distributed strategy for storable liquid fuel production, with transport of stored liquid product to a centralized processing/upgrading conversion facility. This would address some fundamental drawbacks with long-distance transport of typically bulky biomass feedstocks to large centralized biomass conversion facilities. The potential commercial advantage would be the ability of pyrolysis to “densify” raw biomass to pyrolysis oil at distributed, remote locations. This may make pyrolysis oil upgrading an option for locations where the biomass resource is scattered and hard to consolidate.

Future research needs for pyrolysis and pyrolysis oil upgrading should focus on the following areas:

- **Better understanding of pyrolysis reactions:** The production of bio-oil from pyrolysis involves a very complicated set of reactions that are not well understood. Figure 7-2 below, from Iowa State University², shows a spectra demonstrating the vast range of compounds present in bio-oil.

² Iowa State University, Center for Sustainable Environmental Technologies, available at <http://www.cset.iastate.edu/research-projects/product-distribution-from-fast-pyrolysis-of-biomass.html>

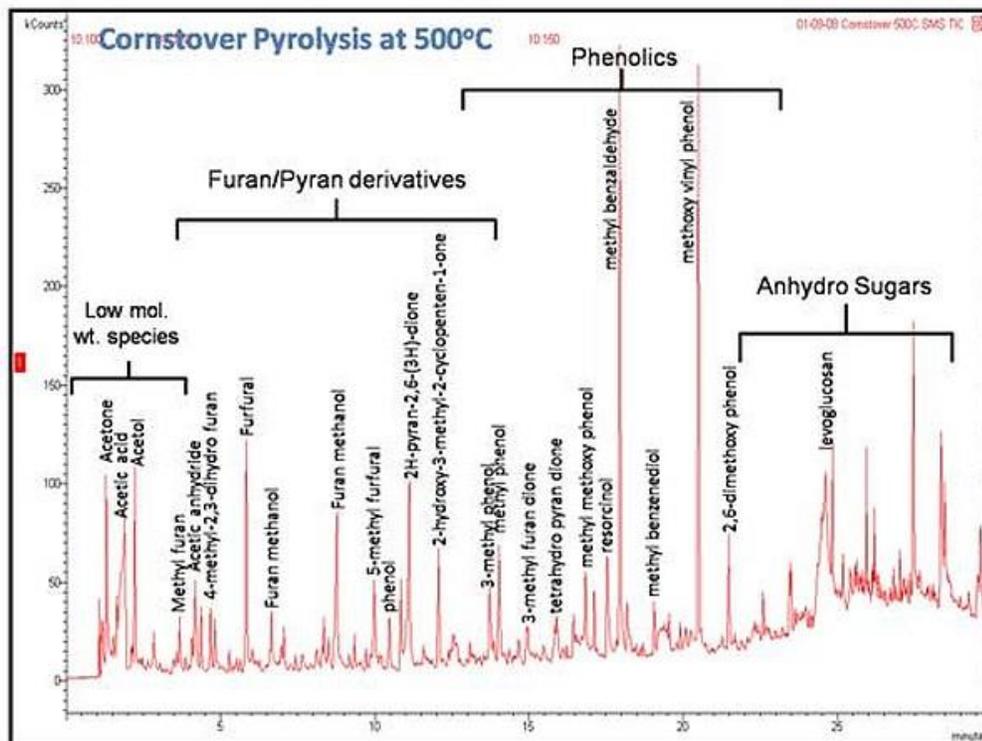


Figure 7-2. Spectra of Compounds in Bio Oil.

The key reactions that drive the bio-oil synthesis have not been thoroughly documented, making it difficult to optimize reactor configurations and conditions. Understanding the chemistry better would allow better designs of small scale units that could eventually be turned into more efficient commercial demonstrations.

- **Catalytic (in-situ) pyrolysis:** Noncatalytic pyrolysis does not produce fungible gasoline and diesel products that can be used in the transportation infrastructure. When catalysts are used in pyrolysis, alkylation, isomerization and reforming reactions can take place to produce alkanes and aromatic and cyclic compounds, major components of diesel and jet fuel. Multifunctional catalyst systems that can perform this step in the conditions present in a pyrolysis reactor need to be developed.
- **Improve upgrade catalyst formulations and reduce hydrogen requirements:** Commercially demonstrated upgrading efforts use two main steps to produce fungible fuels: a first step that deoxygenates the oil and reduces the acid number, and a second that changes the molecular composition closer to that of fuel quality. The petroleum refining industry continues to look at ways to develop upgrading catalysts that can improve yields and be more tolerant of poor quality feedstocks. Future research in this area not necessarily related to pyrolysis oils could be of benefit to the commercialization of this technology.
- **Upgrading bio-oil using syngas derived from biomass gasification:** Hydrogen is expensive and using hydrogen for bio-oil upgrading is typically not economic at a stand-alone pyrolysis oil facility. To operate a stand-alone pyrolysis plant, it may be necessary to

build a small gasifier to supply syngas to the adjacent pyrolyzer to achieve self-sustained operation. Using syngas as a hydrogen source for bio-oil hydrotreating has not been explored. The interactions between CO and bio oils are not well understood. CO may help enhance molecule chain length, which may be beneficial for diesel production.

- **Enhancing the feedstock flexibility of pyrolysis units:** Most pyrolysis reactors need dry, consistent feedstocks which have undergone pre-processing to the reactor. Improving reactor performance to allow a wider range of feedstock types and reducing sensitivity to size and content would lower the cost of raw materials and improve yield. In addition, reliability would be improved by reducing reactor fouling.
- **Effect of alkaline cations in biomass feedstock:** The alkaline cations in biomass serve as a catalyst for reactions in the pyrolysis process. While this result is understood empirically, little work has been done on the intentional manipulation of these alkaline cations. Instead, research has largely focused on examining how their naturally varying levels impact bio-oil properties. There is a need for a more systematic understanding of the role of different alkaline cations, as well as the alkaline cation concentration, on the pyrolysis reaction. The introduction of different catalytic materials could be used to alter the product bio-oil composition.
- **Continue research on novel upgrading strategies, such as microwaves:** Most of the enhancements to existing hydrotreating and catalytic upgrading methods are likely to be incremental, given the level of catalysis research performed to date. More novel upgrading methods have the potential to make major step changes in the cost or equipment required to perform upgrading more likely.

Pyrolysis is part of the suite of thermochemical technologies that PIER should allocate research funds towards. The smaller-scale, less expensive nature of pyrolysis in comparison to other thermochemical process provides useful advantages that help offset the poor quality of the pyrolysis oils that are produced. The potential of utilizing pyrolysis to “densify” raw biomass to pyrolysis oil at distributed, remote locations, which can subsequently be transported to a centralized processing/upgrading conversion facility, appears to merit further investigation. Economic analyses of the viability of such a strategy could be tied to the study recommended above on identifying optimal facility locations based on feedstock distribution. The upgrading of product oils to transportation-quality liquid fuels is the most significant technical challenge for pyrolysis and it is suggested that this be the primary emphasis of any pyrolysis research funding. The petroleum industry continues to look at ways to develop upgrading catalysts that can improve yields and be more tolerant of poor quality feedstocks. Some strategies that could be used to facilitate upgrading include utilizing syngas from a small gasifier, in-situ catalytic pyrolysis, or the development of more novel upgrading methods, such as microwave techniques.

8 Hydrogenated Renewable Diesel and Jet Fuel

8.1 Introduction

Renewable diesel fuels can also be produced via more traditional refinery approaches such as hydrotreating. Hydrogenated renewable diesel can be produced with a hydrotreating unit that is dedicated to the processing of only vegetable or animal oil feedstocks or where oils or fats are coprocessed with the diesel distillate fractions derived from petroleum. For a dedicated facility, the fuel properties of hydrogenated diesel are similar to those of a synthetic GTL or Fischer-Tropsch fuel. These can meet the ASTM-D975 specifications for diesel fuel, and hence could be used within the existing infrastructure for blending and transporting diesel fuels. Since both biodiesel and hydrogenated renewable diesel can be manufactured from vegetable oil, animal fat or other biomass, hydrogenated renewable diesel can also be called second generation biodiesel. In this chapter, the technical development and ongoing research for hydrogenated renewable diesel as a transportation fuel are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for hydrogenated renewable diesel are provided.

8.2 Development of Hydrogenated Renewable Fuels for Transportation Applications

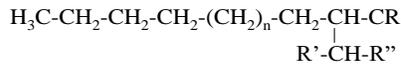
8.2.1 *Hydrogenated Renewable Diesel Feedstocks*

The feedstocks for the hydrogenated renewable diesel include vegetable oils and other oils similar to those used in biodiesel production, as discussed in section 4.2. It is possible that there may be more constraints on the feedstocks that could be used for jet fuel production via a hydrotreating process, or that the feedstock would need to be more homogeneous than would otherwise be needed for renewable diesel fuel production.

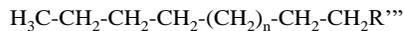
8.2.2 *Hydrogenated Renewable Diesel and Jet Fuel Production*

Hydrotreating is a process typically used to remove sulfur impurities from diesel fuel. By adding hydrogen instead of the methanol typically used in biodiesel production, the process eliminates the oxygen normally found in biodiesel, leaving a hydrocarbon mixture of isoparaffins (branched chain hydrocarbons, see Figure 9-1) and normal paraffins (straight chain hydrocarbons, see Figure 9-1) that is similar to conventional diesel.

Isoparaffins



Normal Paraffins



Where:

n = number of CH₂ groups

R, R', and R'' = additional iso or normal paraffin structure

R''' = additional normal paraffin structure

Figure 8-1: General structure of Isoparaffins and normal paraffins

Hydrogenated renewable diesel fuels are either produced or developed by a number of commercial companies. This includes companies that are directly hydrotreating vegetable oils and companies that are coprocessing vegetable oils with petroleum diesel feedstocks.

Some of the companies currently involved in the area of renewable diesel include:

- Neste Oil with its NExBTL fuel;
- BP's work on extracting oils from plants and combining them with refinery streams that are being hydroprocessed, as well as the hydrogenation of animal fats to produce a diesel blending component;
- Petrobras H-BIO process;
- Nippon Oil work with hydrogenated palm oil;
- UOP's Ecofining™ process in conjunction with Eni SpA;
- CanmetENERGY SUPERCETANE Technology.

Neste Oil has one of the most advanced renewable diesel programs (Neste Oil 2010; Kureonen et al., 2007). Neste Oil is based out of Finland and is 50% owned by the Finnish government. The company uses a process known as NExBTL (Next generation Biomass To Liquid) diesel technology. The process utilizes an integrated separate unit for hydrotreating vegetable oils. The unit includes pretreatment, hydrogenation, and a further conversion process in order to get a pure hydrocarbon end product. Neste Oil has two renewable plants at its location in Porvoo, Finland that began operations in 2007 and 2009, respectively. These plants both have a capacity of 190,000 tons/year. Two larger refineries, with annual production of 0.8 million tons each, are being built in Singapore and Rotterdam, to be completed by 2010 and 2011, respectively.

ConocoPhillips (2006) has been hydrotreating a co-processed mixture of soy oil and diesel fuel in a refinery in Ireland since late 2006. They also planned a partnership with Tyson Foods with

this same process to use tallow in several of its US refineries. The partnership with Tyson Foods was canceled, however, when the subsidy for green diesel was cut from \$1.00 to \$0.50 per gallon (Biofuels Digest, 2009). Tyson Foods is reportedly still going ahead with a 75m gal/year biofuels plant in Louisiana in joint venture with oil company Syntroleum, with the plant expected to start up in 2010. Valero Energy and Darling International, a US tallow and grease producer, are also planning a joint venture to build a 135 million gallons/year renewable diesel production facility on a site adjacent to Valero's St. Charles refinery in Louisiana (Green chemicals, 2009). The plant will use waste grease and maybe other feedstock.

Petrobras (2010) is a Brazilian company that has developed the H-BIO process for utilizing renewable oils in their diesel fuel production plants. This process involves a catalytic hydroconversion of the mixture of diesel fractions and vegetable oil in an HDT reactor under controlled conditions of high temperature and hydrogen pressure. The triglycerides from the vegetable oil are transformed into linear hydrocarbon chains, similar to that already existing in the diesel coming from petroleum. The most important aspect of the H-BIO process is its very high conversion yield, at least 95% v/v to diesel, without residue generation and a small propane production as a by-product. A schematic of the process is provided in Figure 9-2.

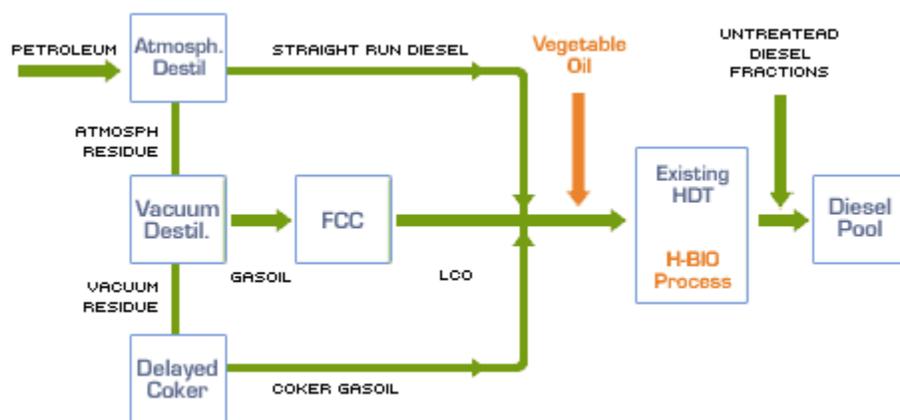


Figure 8-2. H-Bio Process Schematic

According to their website, Petrobras (2010) was evaluating putting the H-BIO process in three refineries by the end of 2007 with vegetable oil consumption around 256,000 m³ per year, corresponding to 10% of the Brazilian soybean oil exportation in 2005. The addition of the H-BIO process in the other two Petrobras refineries was planned for 2008, which would have increased the total vegetable oil consumption to about 425,000 m³ per year, which would be equivalent to 16% of 2005 Brazilian soybean oil exportation. The investments expected to be required for these programs were \$38 and \$23 million, respectively, for the 2007 and 2008 programs.

Nippon Oil Corporation, in conjunction with Toyota Motor Corporation, Hino Motors, and The Tokyo Metropolitan Government have evaluated renewable diesel fuel produced by hydrogenating a vegetable oil feedstock (Iki et al., 2006). Nippon Oil explored reaction temperatures ranging from 240°C to 360°C, with reaction pressures of 6MPa and 10MPa, and used a common hydrodesulfurization catalyst. The resulting fuel is aromatics- and sulfur-free,

with a high cetane number (101). It also has a higher calorific value (MJ/kg) than biodiesel and conventional petroleum diesel. The hydrogenated palm oil showed good oxidation stability in accelerated oxidation testing, but a higher cloud point than palm biodiesel. In testing in a 2.0-liter engine, the hydrogenated palm oil resulted in a 22% decrease in total hydrocarbons, a 15% reduction in CO, and an 11% decrease in PM, but an increase in NO_x.

UOP, a subsidiary of Honeywell, in conjunction with European refiner Eni S.p.A. have been developing a production facility to produce “green diesel” from various vegetable oils (CleanTech Group, 2007). The catalytic hydroprocessing production process is called Ecofining™ and it produces a diesel fuel with a cetane number close to 80 with a cloud point that is more consistent than for biodiesel. It is also being used for the production of jet fuel, as discussed below. The facility, to be located in Livorno, Italy, will process an initially modest amount of oil, up to 6,500 barrels per day, to produce a high-cetane value diesel fuel. The facility was expected to be operational in 2009.

CanmetENERGY, a Canadian company, has also developed a process that utilizes hydrotreating to process vegetable oils into a high cetane number diesel fuel (CanmetENERGY, 2010). The process technology is called SUPERCETANE™ and is shown schematically in Figure 9-3. CanmetENERGY has constructed a 0.2-barrel/day process development unit (PDU) to produce sufficient volumes of SUPERCETANE™ for engine and exhaust emission tests. The PDU complements a semi-pilot plant unit (700 mL tubular reactor) also located at CanmetENERGY. The SUPERCETANE™ process has also been successfully tested in a one-barrel/day hydrotreating pilot reactor at the CanmetENERGY research facilities using depitched tall oil (DPTO) as feedstock.

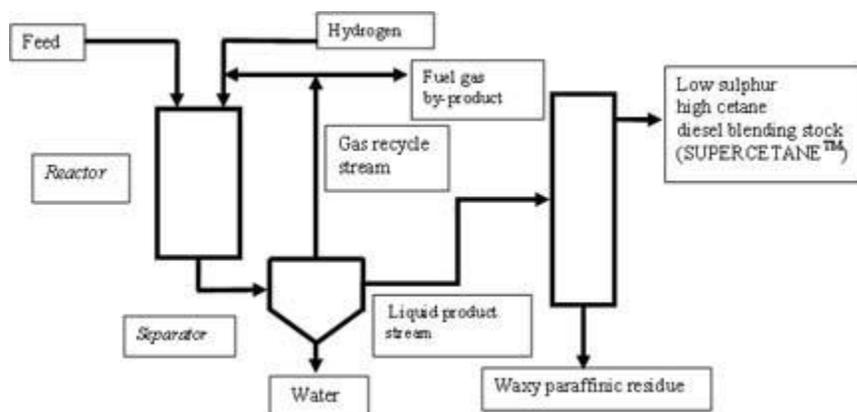


Figure 8-3. A Schematic of the CanmetENERGY SUPERCETANE™ Process

The CanmetENERGY process generates a hydrocarbon liquid with co-products being burner gas and water. The hydrocarbon liquid can be distilled into three fractions: naphtha, middle distillate (CanmetENERGY SUPERCETANE™) and waxy residues. The middle distillate (SUPERCETANE™) is the primary liquid product and yields of 70-80% (by weight) and 85-93% (by volume) have been achieved for yellow grease and tallow. Approximately 3800 liters

of SUPERCETANE™ was produced from DPTO for emission testing at Environment Canada in Ottawa, Ontario and for road tests with Canada Post in Vancouver, BC.

Virent Energy Systems of Madison, WI has developed a fuel production process that utilizes aqueous phase reforming (APR) integrated in with other catalytic hydrotreating and catalytic condensation processes (Blommel and Cortright, 2008). Here, the hydrogenation is used to upgrade aqueous solutions of complex sugars (C₅ and C₆ sugar mixtures) or biomass hydrolysate prior to processing in the APR reactor. In the APR reactor, the oxygenated hydrocarbons react with water over a heterogeneous catalyst to form H₂, CO₂, alcohols, ketones, aldehydes, and byproduct alkanes, organic acids, and furans. The APR process operates at moderate temperatures (450 to 575K) and pressures (10 to 90 bar). The hydrogen generated in this process is then used for the defunctionalization of the highly reactive carbohydrates to a less reactive mono-oxygenated species. The products from the APR can be used to produce a variety of products, including gasoline using a zeolite-based process, jet and diesel fuel using a base catalyzed condensation route, and a high octane fuel using a dehydration/oligomerization route.

8.2.2.1 Hydrogenated Renewable Jet Fuel Production

The production methods being considered for biomass based jet fuel are hydrotreatment of oils and fats and gasification followed by Fischer-Tropsch processing. There are a number of companies engaged in the development of production facilities and commercial arrangements for renewable jet fuel, as discussed in the following. The information below is summarized from Lane (2010).

A number of programs and companies are utilizing Honeywell's UOP process for the development of renewable jet fuel. A summary discussion of these programs is provided below:

- AltAir Fuels, a Seattle-based company, is developing a new facility in Anacortes, WA, based on the technology developed by UOP LLC. The facility will have a nameplate capacity of 100 million gallons per year and is slated to begin operations in 2012. At full capacity, this facility would replace about 10 percent of the petroleum fuel consumed annually at Seattle-Tacoma International Airport, reducing carbon emissions by about 14 billion pounds over 10 years. The feedstock used for this fuel will be camelina oil sourced from Montana-based Sustainable Oils, which has the largest camelina research program in North America and production contracts with numerous farmers and grower cooperatives. Camelina, a nonfood rotation crop similar to soybean and mustard. AltAir Fuels has also signed a Memorandum of Understanding (MOU) with 14 major airlines from the United States, Mexico, Canada and Germany for the purchase of up to 750 million gallons of renewable jet fuel (AltAir Fuels, 2010). The participating airlines include, American Airlines, Air Canada, Alaska Airlines, Atlas Air, Delta Air Lines, FedEx Express, Hawaiian Airlines, Jet Blue Airways, Lufthansa German Airlines, Mexicana Airlines, Polar Air Cargo, United Airlines, UPS Airlines, and US Airways.
- According to UOP, a total of 600,000 gallons of renewable jet fuel was ordered by the military for delivery in 2009 and 2010 in a series of contracts issued by the Defense Energy Support Center (DESC). Cargill and Sustainable Oils are to provide jet fuel made from rendered animal fats and Camelina, respectively, to the air force. Sustainable Oils

has will provide 40,000 gals of Camelina-based jet fuel for the Navy's certification testing program of alternative fuels, with an option for an additional 150,000 gals. One of the factors for selecting camelina was the fact that it has been successfully tested on a commercial airline test flight. Solazyme with partner with UOP to provide the US Navy 20,000 gallons of renewable algae-derived F-76 Naval distillate fuel. Solazyme will also provide up to 1500 gallons of fuel from algae.

- Boeing, Mexico's Airports and Auxiliary Services agency and Honeywell's UOP have a partnership to develop sustainable aviation biofuels sources in Mexico. Sources that will be assessed as part of this partnership include halophytes, algae, Jatropha, and castor.
- In January 2010, "The Masdar Institute of Science and Technology, Boeing, Etihad Airways and UOP Honeywell announced the UAE's first Sustainable Bioenergy Research Project (SBRP) using seawater and the desert for bio-energy in Abu Dhabi. The project will be the first demonstration of the commercial viability of using integrated saltwater agriculture to provide biofuels for aviation. The Sustainable Bioenergy Research Project has a five-year timeline."
- Boeing, UOP, and the Sustainable Aviation Fuels User Group (SAFUG) announced in October 2009 a project to examine the potential for large-scale biofuels production from salicornia bigelovii and saltwater mangroves – plants known as halophytes.
- Scientists at Michigan Technology University, in collaboration with UOP researchers, have evaluated well-to-wheel LCA of GHG emissions from alternative jet fuels. The results showed bio-derived synthetic paraffinic kerosene (Bio-SPK), made from jatropha and camelina oils using the UOP renewable jet fuel process, produced 65% to 80% less GHG emissions compared to petroleum derived jet fuel. Preliminary results also showed that jet fuel derived from camelina oil exhibited one of the largest greenhouse gas emission reductions among biomass based feedstocks.

Several on-going projects are focusing on the development of renewable jet fuel from Algae. Some of these projects include those discussed below. Additional information on algae-based fuels is given in Chapter 9.

- The Defense Advanced Research Projects Agency (DARPA) recently awarded Science Applications International Corp. \$25 million to develop an algae-based jet fuel for use by the US military. The target price for this fuel is \$3/gallon.
- The National Agency for Science, Technology and Research's Institute of Chemical and Engineering Sciences instituted a 12-month project with the aerospace and defense contractor EADS to develop renewable jet from algae in February 2010.
- Sapphire Energy is developing an affordable, scalable open pond algae production system. At the same time it is performing research to identify algae strains with the optimal combinations of high energy output, fast reproduction, and the ability to survive in the open ponds.
- The Natural Resources Defense Council is planning to perform a lifecycle analysis of CO₂ emissions and the socio-economic impact for algae.

Several on-going projects are focusing on the development of renewable jet fuel from jatropha. Some of these projects include:

- JatropaBioJet Corporation of California has formed a World Biojet Alliance (www.biojetalliance.org), a worldwide industry non-profit trade group to serve the needs of the Bio Jet Fuel sector. JatropaBioJet Corporation is the founding charter member of the World Biojet Alliance and has provided funding for its formation. The World Biojet Alliance was founded to “promote, conduct research, coordinate communications and provide solutions for advanced biofuels used in aviation.”
- BioJet Corporation (Biojet, 2010), a Nevada company, entered into a letter of intent with E85 LLC in September 2009, for the sale by BioJet to E85 of 4 million barrels of aviation bio jet fuel. The fuel, known as Bio-SPK for bio-derived synthetic paraffinic kerosenes, will meet ASTM specifications for jet fuel. BioJet expects Jatropa to be the primary aviation biofuels feedstock in the short term.
- The Strategic Technology Office (STO) of the Defense Advanced Research Projects Agency (DARPA) is sponsoring research on converting crop oil to a JP-8 surrogate (STO, 2010a). The goal is to develop an affordable and highly efficient process of converting crop oil to JP-8 surrogate with a minimum 60% conversion efficiency, by energy content, and identify development opportunities to achieve 90% efficiency. They are also sponsoring research to develop affordable alternatives to petroleum JP-8 from agricultural and aquacultural feedstocks that are non-competitive with food sources (STO, 2010b).
- The Sustainable Aviation Fuels User Group (SAFUG) announced a research projects in 2008 to complete the first lifecycle analysis of CO₂ emissions and the socio-economic impact of *Jatropha curcus*.

Other projects to develop renewable jet fuel are as follows:

- KLM conducted a flight test in December 2009 partly powered by a biofuel produced from Camelina. It was the first time passengers were on board a biofuels demonstration light. KLM has announced they have formed a joint venture company called SkyEnergy to develop sustainable biofuels together with North Sea Petroleum and Spring Associates.
- Personnel at the Wright-Patterson Air Force Base are actively involved in direct research and certification of synthetic and biomass-derived alternative aviation fuels (Graham, 2010). On 3/25/2010 a 50/50 mix of conventional JP-8 and a biomass fuel derived from Camelina, a nonfood rotation crop similar to soybean and mustard was flight tested in an A-10C Thunderbolt II.
- Amyris Biotechnologies and the University of Queensland signed a research agreement in February 2010 to explore the conversion of Australian sugar cane into renewable jet fuel.

8.2.3 *Hydrogenated Renewable Diesel and Jet Fuel Distribution and Utilization*

Hydrogenated renewable diesel has a chemical structure similar to petroleum-based diesel, in contrast to biodiesel that is derived by the transesterification processes. Hydrogenated renewable diesel can be used alone or blended with petroleum diesel. Hydrogenated renewable diesel can be used in the existing pipelines, refueling stations and vehicles using conventional diesel. In addition to the fuel infrastructure, hydrogenated renewable diesel can be manufactured utilizing the current refinery infrastructure as well. Other advantages of using hydrogenated renewable

diesel as a transportation fuel include its high cetane number, its low aromatic content, and its ultra-low sulfur content, which provide vehicle performance with lower emissions than traditional petroleum diesel fuels.

The hydrogenated renewable jet specification is currently under development. There are a number of companies working on/toward a specification for renewable jet fuel and doing characterization studies on renewable jet fuel. These activities are summarized below.

There is one basic specification in development for a bio based jet fuel, namely Bio-SPK (Bio-Derived Synthetic Paraffinic Kerosene), which is expected to receive final commercial flight approval this year. It is made primarily from virgin oils such as algae, Jatropha, or Camelina, but waste biomass is expected to be a major factor in the future. The major process employs the UOP Honeywell hydrotreatment process to convert the oils to renewable jet fuel. The major suppliers of the oils are Solazyme, Sustainable Oils, Sapphire Energy, and Terasol.

Dynamic Fuels produces renewable jet from animal fats and vegetable oils using their R-8 Bio-Synfining process. The Air Force Research Laboratory tested 600 gallons of R-8 and reported: “initial physical property and T63 engine testing indicates R-8’s performance as indistinguishable from that of S-8, Syntroleum’s Fischer-Tropsch synthetic jet fuel that first flew in 2006 aboard the B-52. Additional tests of R-8 are underway, with the product also entering the first stages of the MIL-HDBK-510 Alternative Fuel Certification Process.”

8.3 Technical Limitations and Commercialization Gaps for Hydrogenated Renewable Diesel and Jet Fuel

8.3.1 Feedstocks Limitations

The high cost of feedstock oils used for hydrogenated renewable diesel relative to crude oil is one of the main limitations for the development and commercialization of this technology. Another key consideration is the potential impact of using food crops for fuel production. These issues are similarly to the limitations for biodiesel, and the impacts of these limitations are discussed in greater detail in chapter 4. With the tighter specifications of jet fuel, it may be more sensitive to feedstock inhomogeneity than other hydrogenated diesel fuels.

8.3.2 Production Limitations

The hydrotreating process used for production of these renewable diesel fuels is a mature technology and is not a limitation to commercialization. The primary limitation for production is the cost. The capital costs for a hydrotreating plant are higher than those for comparable processing of vegetable oils to biodiesel, and hence the hydrogenated renewable diesel fuel is at a corresponding disadvantage relative to biodiesel. The availability of excess capacity for hydrotreating in existing refineries will be another important consideration. While some existing refineries have excess capacity for hydrotreating, the hydrotreating capacity of other refineries is either just sufficient or even below the capacity needed to meet the existing production needs of the refinery. The coupling of the high feedstock costs with these production costs has made the commercialization of hydrogenated renewable diesel not cost competitive in the U.S. to date. As

discussed above, hydrogenated renewable diesel fuels have enjoyed some level of success in Europe and other countries, but this is due to more favorable economic considerations, such as high fuel costs or government incentives. It is possible that some additional market opportunities might also be available for jet fuel, given its more unique and stringent properties and market.

8.3.3 *Distribution and Utilization Limitations*

Hydrogenated renewable diesel has similar properties to that of more traditional petroleum diesel. As such, there are not significant limitations to utilizing the fuel within the existing diesel fuel infrastructure, as long as the fuel meets all existing fuel specifications. In the case of renewable jet fuel, specifications are currently under development, as discussed in section 6.2.3 and 8.2.3.

8.4 **Environmental and Other Considerations**

CARB’s (2009a, 2010) Well to Wheel GHG emissions for various scenarios of biodiesel production using the CA-GREET version 1.8b are provided in Table 9-1. The results show that the renewable diesel produced from the conversion of tallow would provide significant reductions in carbon intensity values. The carbon intensity values for the higher energy rendering process are higher than those values obtained for biodiesel production from waste oils, as discussed in chapter 4.4. The carbon intensity values for the lower energy rendering process are slightly higher but are more comparable to those values obtained for biodiesel production from waste oils. The carbon intensity values for renewable diesel production from soybeans provide some benefits in carbon intensity relative to the baseline diesel, but the benefit is much smaller due to the assessed land use effects.

Table 8-1: Adjusted Carbon Intensity Values for Diesel Fuel and Renewable Diesel Fuel.

Fuel	Pathway Description	Carbon Intensity Values (gCO ₂ e/MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Diesel	ULSD – based on the average crude oil delivered to California refineries and average California refinery efficiencies	94.71	0	94.71
Renewable Diesel	Conversion of tallow to renewable diesel using higher energy use for rendering	39.33	0	39.33
	Conversion of tallow to renewable diesel using lower energy use for rendering	19.65	0	19.65
	Conversion of Midwest soybeans to renewable diesel	20.16	62	82.16

Renewable diesel fuels generally provide emissions benefits in comparison with petroleum diesel, including CARB-certified diesel, due to their favorable properties of high cetane and low aromatics (Rothe et al. 2005; Kleinschek 2005; Aatola et al. 2008; Kuronen et al. 2007). As part of the development of the LCFS, the University of California at Riverside evaluated the emissions of renewable diesel fuel compared with those of a CARB-certified diesel on a 2006 Cummins ISM 370 (Durbin et al., 2009). These results showed that NO_x emission decreased with

increasing levels of renewable diesel, with the emissions reductions ranging from approximately 3 to 18% depending on the testing condition and the blend level. Combinations of renewable diesel with biodiesel were found to be a viable strategy for mitigating the biodiesel NO_x increase, but generally a ratio of 3 or 4 parts renewable diesel to 1 part biodiesel was needed to achieve a NO_x neutral blend. It is expected that the emissions differences between petroleum-based jet fuel and renewable jet fuel would be less given the tighter specifications of jet fuel, although there might be some differences for specific unregulated species.

8.5 On-going Research

Direct hydrotreating of animal fats and vegetable oils is done in either a unit built specifically to process bio-oils or mixed with conventional diesel prior to the refinery hydrotreater. Several companies are at various stages of commercializing this production process. The current status of the efforts of these companies is discussed below.

8.6 Recommendations for Hydrogenated Renewable Diesel and Jet Fuel

Hydrogenated renewable diesel fuel or jet fuel offers some interesting advantages as an alternative transportation fuel. Renewable diesel fuel utilizes the technically mature petrochemical process of hydrotreating and produces a fuel that has characteristics similar to those of diesel fuel, making it compatible with the existing petroleum infrastructure. While this fuel has seen some level of commercialization in Europe, the process is still not economically viable in the US. This is due to the higher cost of vegetable oil-based feedstocks compared to crude oil and the higher costs of hydrotreating compared to the biodiesel esterification process. Consequently, our research recommendation for hydrogenated renewable diesel fuel focus on providing cost reductions in feedstocks and production. These same research recommendations would also be equally application to the production of renewable jet fuel.

The development of new/lower cost feedstocks is probably the most critical area of research for renewable diesel fuel. Advances in feedstock development would also provide benefits to the development of biodiesel as well, so research in this area would have broader benefits. Jatropha is an example feedstock that can be grown on marginal lands and is the subject of various research efforts. Similar to biodiesel, all new feedstocks would need to be well characterized. For renewable diesel production, some of the most important properties would be impurities and the extent to which the feedstock would need to be preprocessed. Similarly, the necessity for other production modifications to make a quality fuel end product would also need to be studied.

The production of diesel fuel from hydrogenated vegetable oils is a process that is mature and being carried out at a commercial scale in Europe and Brazil. Improvements in the stand alone processes would be largely incremental rather than major breakthroughs. Some areas where production improvements could be made are in improving the activity and stability of the catalyst, understanding the influence of contaminants in the processing and controlling issues such as corrosion. Some fundamental research in characterizing the exothermal properties of the process reactions is also being conducted (IFP, 2010). Another option that is being studied is Co-hydrotreating vegetable oils with more traditional refinery streams (Huber, et al., 2007; Lappas, et al., 2009). This could potentially provide a lower cost option for introducing hydrogenated

vegetable oils into diesel fuel. This would require some modifications within existing refinery operations. Such co-processing would likely impact the durability of the hydrotreating catalyst, so this is an issue that needs to be investigated. The development of hydrotreating catalysts that are sufficiently robust to handle blends of petroleum fractions and vegetable oil is one potential area for research funding. Similarly, pretreatment processes may also be needed to facilitate co-processing of vegetable oils and diesel fractions (Lappas, et al., 2009).

9 Algae-Based Fuel Production, Feedstocks, and Distribution

9.1 Introduction

There are a number of characteristics that make algae attractive as a potential feedstock for the production of biofuels. Algae fuel, also called algal fuel, is a biofuel that is derived from algae. The precursor to Algal fuel is produced when algae convert light energy into chemical energy whereby carbon dioxide and water are converted into organic molecules (biomass). One of the major advantages of algae is that it does not compete directly for land and resources that could otherwise be used to grow crops for food. Algae can survive in water with high salt content and use water that would otherwise be deemed unusable. With recent controversies regarding the use of agricultural land to produce crops for biofuels, these traits offer a significant advantage over traditional oil seed crops for biofuels production.

High projected yields per acre are another reason that algae have been identified as an attractive feedstock for biofuels production. Fast growth rates and high oil content mean that algae can potentially produce 10 times or more lipids (oils) per acre than soybeans or other oil seed crops. With continued development, it may be possible to produce algae that have up to 70 percent of its mass in the form of usable oils, and this combined with the fast growth rates could lead to a high biological efficiency. Current projections estimate that 6,000 to 15,000 gallons of biofuel per acre of algae may be achievable.

In this chapter, the technical development and ongoing research for algae as a transportation fuel are reviewed, its technical and environmental limitations and commercialization gaps are discussed, and the research roadmap funding recommendations for algae are provided.

9.2 Development of Algae-Based Fuels for Transportation Applications

9.2.1 Algae Feedstocks

Algae have relatively simple structures, fast growth rates, and high oil contents (for some species). Algae are classified into two broad types: macroalgae and microalgae. Macroalgae are large aquatic photosynthetic plants that can be seen without the aid of a microscope. Microalgae are subdivided into two broad categories: the prokaryotic (no nucleus) cyanobacteria and the true eukaryotic (true nucleus) algae. The prokaryotic cyanobacteria are often referred to as the blue-green algae. There are thousands of different alga species in the world. Research into algae for the mass-production of oil is mainly focused on cyanobacteria and eukaryotic microalgae.

While cyanobacteria and microalgae have been the major focus, there is some research on macroalgae (Aresta et al., 2003; Aresta et al., 2004; Ross et al., 2008a). Aresta et al. (2003, 2004) studied some Mediterranean algae and used supercritical CO₂ extraction and organic solvent extraction to obtain biofuel. Ross et al. (2008b) studied five macroalgae native to the British Isles and used thermogravimetry and pyrolysis-gas chromatography-mass spectrometry to evaluate the production of fuel. Thermogravimetry measures the loss in weight as a sample is heated in a nitrogen atmosphere which provides a measure of the quantity of volatiles evolved as a function of temperature. Higher weight loss at lower temperatures indicates a higher volatility, and

therefore a more combustible, sample. Analysis of the products of pyrolysis by gas chromatography-mass spectrometry provides a measure of the various types of chemicals produced and therefore it is possible to estimate the likelihood of producing usable fuels from these chemicals. The authors concluded that because of the high ash content of the macroalgae, it could not be processed by gasification but it could be processed by pyrolysis to generate fuel. The high ash content is due to the much higher concentration of metals, particularly sodium and potassium, for macroalgae compared to terrestrial algae. When the algae is gasified or pyrolyzed the metals are non-combustible and thus are left as a solid mass (ash).

9.2.2 *Algae Production Processes*

9.2.2.1 Production Background

Algae are already grown commercially in some parts of the world, primarily for the production of food, dyes and pharmaceuticals. Open systems such as raceway-type ponds have commonly been used in the cultivation of algae for these types of operations. However, open systems can be susceptible to contamination by invasive strains of algae or other microorganisms. This tends to limit the types of algae that can be effectively cultivated in open ponds and raceways. For this reason, closed systems such as photobioreactors (PBR) have been investigated for the production of algae for biofuels. PBRs are transparent vessels which allow light in and essentially act like a greenhouse preventing contamination and water losses due to evaporation. However, capital costs for these closed systems are much higher compared to open systems and at this time it appears unlikely that these systems will be economical in the near term. It may be more likely that advances in breeding and genetics will lead to more robust strains where closed systems are not needed.

Algae can be useful in the treatment of waters polluted with organic matter, excess nutrients (e.g., nitrogen, phosphorus, potassium), metals, synthetic organic compounds, and potentially endocrine disrupting compounds (such as human hormones and antibiotics from animal facilities). Major types of wastewaters available for integrated wastewater treatment and algae production are municipal, organic industrial (e.g., food processing), organic agricultural (e.g., confined animal facilities), and eutrophic waters with low organic content but high nutrient content (e.g., agricultural drainage, lakes and rivers). Research is needed on issues such as nutrient uptake by algae, the ability of algal systems to provide natural disinfection and removal of trace contaminants, and potential issues associated with algae bio-accumulating the heavy metals that are present in some wastewater streams.

In addition, there are some novel approaches to algae cultivation still being investigated and developed. One concept that has gained attention is the idea of using algae to sequester carbon dioxide emissions. Since carbon dioxide is required for algae to grow, the opportunity exists to use algae to capture carbon dioxide emitted from the stack of a fossil fuel fired power plant. Figure 9-1 illustrates the range of input and output streams that are being evaluated and developed for integrated algae production systems.

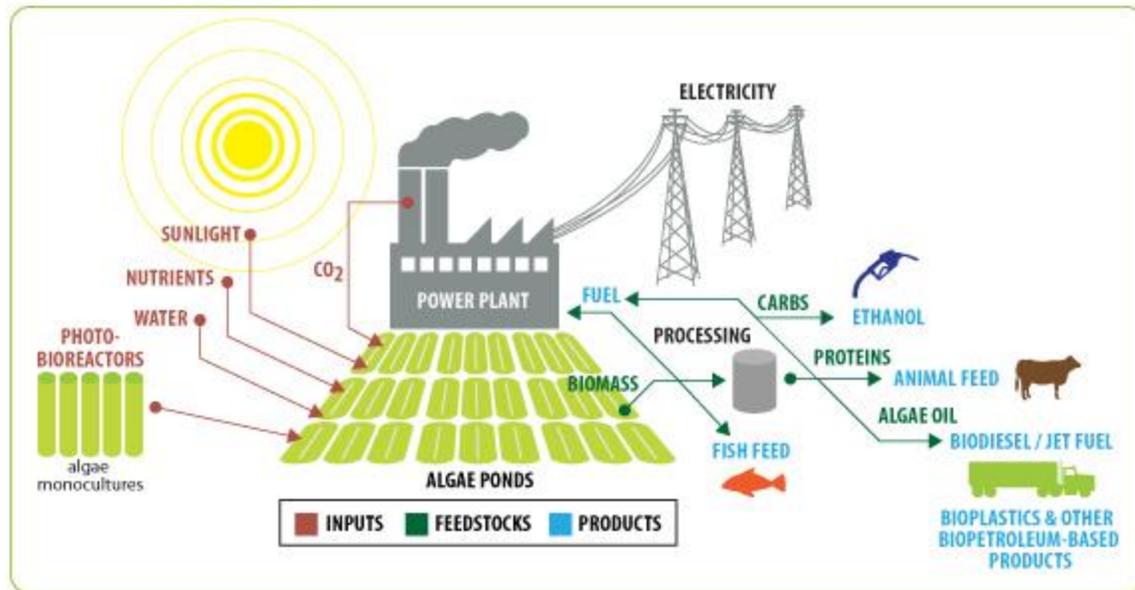


Figure 9-1: Input and Output Streams for a Conceptualized Algae Fed Biorefinery (Source HR BioPetroleum).

9.2.2.2 Historical Development of Algae Research

Algae Research dates back to the 1940's and 1950's. This includes discoveries that many species of microalgae could produce large amounts of lipids under certain conditions and that this phenomenon could be enhanced by the starvation of certain key ingredients. In the late 1950s, several researchers suggested the utilization of the carbohydrate portion of the algae cell for the production of methane gas via anaerobic digestion.

The United States Department of Energy conducted a research program called the Aquatic Species program between 1978 and 1996 (Sheehan et al., 1998). The program represents the most comprehensive research effort in the area of algae fuels to date. Over that period, approximately \$25 million was invested in algae fuels. The program focused on producing biodiesel from algae after initially emphasizing the production of hydrogen. These researchers examined over 3,000 strains of algae from various locations throughout the U.S. They conducted a series of tests to examine their potential to produce lipids and their tolerance to salinity, pH, and temperature to isolate the most promising strains, which were mostly green algae and diatoms. More focused studies were then conducted on these strains to increase their lipid content under conditions where key nutrients such as nitrogen and silicon were deprived. From a production standpoint, the program focused on an open pond system. A pond developed in Roswell, NM achieved yields of up to 50 grams per square meter per day, although low temperatures were found to hamper yields at that location. This program also identified the need for cost effective methods to harvest and dewater the algae.

9.2.2.3 Commercial Development of Algae Production

Interest and investment in algae-based fuels has begun to grow again at a more rapid pace. A number of commercial companies have begun to invest in algae based fuels as follows:

Sapphire Energy (2010) has received \$104.5 million from the government to build an integrated algal biorefinery in Luna County, New Mexico. The algae will be grown in open ponds using high-salinity, brackish water. Construction is expected to begin in September 2010. Sapphire Energy has worked with identifying algae strains with desirable characteristics for production of gasoline, jet, and diesel fuel. Through genetic modifications they have attempted to produce strains with the ability to grow in adverse conditions while producing high yields of the desired precursors to gasoline, jet, or diesel. To aid in the harvesting, they have also attempted to bioengineer strains which would aid in the flocculation, which is the part of the production process where the algae is clumped together for harvesting. To date, these engineered strains require the addition of nitrates to trigger the flocculation, which is not an economically desirable method (Poon, 2010).

On July 14, 2009 ExxonMobil (2010) joined with Synthetic Genomics, Inc. to develop, test, and produce biofuels from algae. ExxonMobil will focus its research efforts on engineering and process development and scale up, determining what type of production systems to utilize to grow algae, upgrading the oils produced by algae into finished products, and total process integration. Synthetic Genomics, Inc. (2010) is a company that specializes in genomic solutions to different global issues. Synthetic Genomics, Inc. will focus its research efforts on biological research for algae strain development, growth and harvesting, determining which type of production systems to use to grow algae, and bio-oil recovery research and development. In addition to the alliance with ExxonMobil to develop algal biofuels, Synthetic Genomics, Inc. is also working with BP on microbial-enhanced hydrocarbon recovery and with the Asiatic Centre for Genome Technology on sustainable agricultural products.

Solazyme (2010), in partnership with Chevron, has been conducting work with heterotrophic algae that can be grown in the dark. The Solazyme process grows heterotrophic algae in industrial fermentation vessels using carbonaceous substrates such as sugars, green waste, or switchgrass as a feedstock. This process, combining genetically modified strains of algae with an uncommon approach to growing algae, is capable of producing as much as 75% of the dry weight of algae as oil, which can provide improved biofuel yields and reduced fuel costs. Solazyme has produced thousands of gallons of algal oil and refined the algal oil into B100 and jet fuel meeting ASTM standards. With significant private investment and a \$21.8 million grant from DOE, Solazyme is going to build its first integrated biorefinery using this process in rural Riverside, Pennsylvania.

Algenol (2010), a Florida based company, has developed a technology called DIRECT TO ETHANOL[®] that uses hybrid algae to produce ethanol from CO₂, water and sunlight. In collaboration with Dow Chemical and with a \$25 million DOE grant, the company is planning to build a pilot-scale biorefinery that will make ethanol directly from CO₂ using hybrid algae in a photobioreactor algal biofuel system. The capacity of the plant will be 100,000 gallons of fuel grade ethanol per year.

Solutions Recovery Services, out of Dexter, MI, has developed a technology for wet extraction of the oils from algae. The technology processes the algae at high temperatures and high pressures with mild acid to separate oil from protein and carbohydrate fractions of the algae. Since this extraction is done as a wet process, not energy needs to be expended on drying the

algal biomass. This technology is currently being employed at an outdoor raceway algal production facility being operated by the Center of Excellence for Hazardous Materials Management in collaboration with other institutions in Eastern New Mexico (FAO, 2010). SRS is also working with NREL/DOE on developing this technology (Morello and Pate, 2010), and a number of other private companies have been working with versions of this technology.

Phycal, LLC (2009) and Algaeventure Systems (2009) are two other companies working in the area of algae production. These companies are more actively involved in the harvesting and utilization of algae, as discussed in greater detail in 8.3.1.

There are many other companies, research labs, and universities which are actively working on various aspects of algae production and harvesting. These research efforts include working with existing strains of algae and genetically engineering new strains to improve yields or to produce specific products. A listing of these entities and a general description of what they are doing is available in a Coordinating Research Council (CRC) report prepared by Hoekman et al. (2009).

9.2.3 *Utilization and Infrastructure of Algae-Based Fuels*

Algal biomass can be converted to many types of renewable fuels including ethanol, butanol, biodiesel, green gasoline, and green diesel, using biochemical conversion and thermochemical conversion technologies. Biodiesel is one of the main potential end products from algae production. The utilization of algae-based biodiesel would be similar to that for biodiesel from other feedstocks, as discussed in section 4.2. Biodiesel is commonly used in diesel engines/vehicles with no modification, so algae-based biodiesel could be readily introduced into the diesel market. For algae processed into a methyl ester biodiesel, it would still have issues with compatibility with the existing pipeline infrastructure, as discussed in section 4.3. Other issues with algae-based biodiesel that should be understood include the propensity to increase NO_x emissions, cold weather properties, and storage stability. Algae-based biodiesel would need to meet the same ASTM D6751 fuel standards as biodiesel from other feedstocks.

Green gasoline fuels and green diesel can be produced from algal lipids by catalytic cracking and upgrading to meet the ASTM standards through hydrotreating processing. Regardless of the feedstocks, algae-derived gasoline and diesel will need to comply with the same ASTM specifications as petroleum gasoline and diesel. As a result, the distribution of algae-derived gasoline and diesel should be compatible with the current infrastructure and should not require any significant modifications. Algae-derived renewable diesel does not have oxidative stability issues like biodiesel produced from vegetable oil or animal fat, meaning it can be stored for longer periods of time compared with biodiesel. Renewable diesel, however, does encounter cold weather problems similar to biodiesel. Another issue with algae diesel is that the types and amounts of contaminants contained in the final product varies by different fuel production processes (DOE, 2009f).

The algae can also be processed as a whole using pyrolysis, gasification, or anaerobic digestion. These technologies are discussed in separate chapters above and below, along with their respective limitations. For the traditional gasification or pyrolysis processes, the algae would

likely require extensive drying to lower the feedstock moisture levels. Alternatively, the algae could be used directly via a steam hydrolysis process.

9.3 Technology Limitations and Commercialization Gaps for Algae-Based Fuels

9.3.1 Feedstock Limitations for Algae-Based Fuels

The primary issues with feedstocks for algae-based fuel production are how effective the different algae strains are in the production process. These issues include the growth rates and photosynthetic efficiency of the strains, their resistance to biological attack, their production levels for oils or lipids, and their ability to grow under a wider range of environmental conditions including wider temperature ranges, and reduced water and nutrient requirements. Photosynthetic efficiency refers to the efficiency of converting CO₂ and water to organic molecules (i.e., carbohydrates, proteins, and lipids) following the absorption of light energy. The production of lipids, which are the main source for producing biofuel, is influenced by other factors such as stress conditions (high light and/or nutrient starvation).

9.3.2 Production Limitations for Algae-Based Fuels

It is clear that before algae-to-biofuel production sees widespread commercialization there is significant research and development that still needs to be done. Although the process of making biofuels from algae is already known and proven, there are obstacles that need to be overcome before the process can be implemented on a commercial scale. Currently, there are no commercial-scale algae production facilities for the production of fuel because the process has not yet been shown to be economically viable. Thus, the primary challenge facing biofuels production from algae is economic. Research is underway to identify the most appropriate strains. Work also continues on refining methods for extracting and processing the oils. Some of the main areas of current investigation include:

- Resistance to biological attack.
- Reduced water and nutrient requirements
- Wider growing conditions, including wider ambient temperatures and under both light and dark conditions.
- Higher percent of total biomass as oil.
- Faster growth, higher biological efficiency.
- Basic research in multi-trophic³, molecular-level algal ecology.
- Improved oil extraction and fractionation (separating the oils into various boiling range fractions) technology.
- Use of algal byproducts after the lipids or other desirable fuel precursors have been extracted.

³ **Integrated Multi-Trophic Aquaculture** (IMTA) is a practice in which the by-products (wastes) from one species are recycled to become inputs (fertilizers, food) for another.

- Lifecycle analysis of energy and carbon in selecting preferred fuel conversion technologies.
- Integration issues and opportunities for algal cultivation facilities co-located with industrial CO₂ sources and/or wastewater treatment facilities.
- Evaluation of economies of scale vs. advantages of decentralized production considering parasitic losses of CO₂ transport.

These areas include both the development/cultivation of algae strains for production and the harvesting and processing parts of production. For the development of algae strains, the resistance of algae to biological attack (crop protection) and nutrient utilization and recycling are among the most important issues that must be addressed. For the production processing, harvesting is probably the most important area for additional technological development.

The US DOE evaluated algae-based fuels as part of the development of a “National Algal Biofuels Technology Roadmap”. This Roadmap was based upon input from participants at the December, 2008 National Algal Biofuels Technology Workshop. The workshop participants concluded “that many years of both basic and applied R&D will likely be needed to overcome the current technical barriers before algal-based fuels can be produced sustainably and economically enough to be cost-competitive with petroleum-based fuels.” Nevertheless, due to the potential advantages of algae fuels, they continue to generate interest as a mid-term transportation fuel strategy that could represent the next generation of fuels that follow those derived from cellulosic ethanol. Fuels produced from algae also have the potential to be “drop in” fuels, i.e., have properties closer to existing petroleum based fuels, and therefore represent a more qualitative advance in fuel technology.

9.3.2.1 Algae Production Cost Estimates

Since cost is a primary limitation in the development of algae-based fuels, it is useful to examine some of the different cost estimates for algae-based fuels and the factors that contribute to the current cost estimates. Currently, there are only a few cost estimates for the production of algal biofuels, and they can differ by orders of magnitude (DOE, 2009f). The lowest cost estimates are in the range of \$840 to \$1680 per barrel. To be competitive with production from crude oil, this cost needs to be reduced to at least \$100 per barrel. Some of the major areas that must be addressed to make algal biofuels economically viable are: (1) culture stability, (2) standardized metrics for system-level productivity analysis, (3) nutrient source scaling, sustainability and management, and (4) water conservation, management, and recycling requirements.

Gokhale et al. (2009) note that 50 – 60% of the cost is for the algal production systems, i.e., the feedstock, and 40 – 50% is for the harvesting systems. To reduce feedstock costs will require some or all of the following: (1) breeding algae to enhance photosynthetic efficiency and increase oil accumulation, (2) reduction of contamination by non-desirable algae, bacteria, viruses, and grazers, (3) removal of growth-inhibiting waste products, and (4) recycling the growth media to reduce environmental impact. The reduction of costs for harvesting systems requires (1) improving the harvesting system, (2) improving the oil extraction processes, and (3) optimizing co-product yields. Most current practices involve destructively harvesting the algae for oil by (1) removing it from the water, (2) breaking it open after it is dried to release the fats

and sugars, (3) using solvents to separate the fats and sugars, (4) evaporating the solvents, (5) and then transforming the fats to biodiesel.

Phycal, LLC (2009) has a trade mark process called Olexal™ which milks the lipid oil from the algae and then returns the algae to the growing pond. They report that algal growth is not impaired by multiple milkings and the pond residence time is reduced three fold (Gokhale et al., 2009). They also report harvesting two times more biomass than is harvested by the destructive process and obtaining 1.4 times as much oil. While it is noted that to make algae cost competitive it is necessary to reduce the oil price from \$1,470/bbl to \$84/bbl, they do not provide estimates for the cost of their current technology.

In March of 2009, Algaeventure Systems (2009) announced they had developed a system for harvesting, dewatering, and drying algae that reduces the cost by over 99%. Typically, algae is harvested by centrifugation or flocculation followed by heating the algae to dry it. Algaeventure uses a superabsorbent polymer fabric belt. The belt moves continuously and the water/algae mixture is pumped onto one end of the belt. The composition of the belt allows the water to flow through the belt leaving the algae on top. Their four foot long prototype can process more than 500 liters/hr on less than 40 watts per hour of run time. The algae are dried by waste heat and the dry algae are scrapped off the belt as it goes over the end roller. Algaeventure compared the cost of their system to the cost of a centrifuge and a preconcentrate centrifuge system. Their cost comparison is shown in Table 9-1.

Table 9-1: Cost comparison of algae harvesting, dewatering, and drying

<i>Process</i>	<i>\$/Ton</i>	<i>\$/Barrel</i>	<i>\$/Gallon</i>
Centrifuge	3,400.00	932.78	22.209
Preconcentrate Centrifuge	875.00	240.06	5.716
AVS HDD	1.92	0.51	0.012

9.3.3 *Utilization Limitations for Algae-Based Fuels*

The utilization limitations for algae-based fuels will depend on the specific fuel end products that are derived from the algae production and processing. This would include biodiesel, synthetic gasoline or diesel fuels, or alcohols depending on the processing. In each case, the final end product fuel would need to meet the applicable fuel standards in place for that specific fuel component. Once the fuels have met the applicable fuel standards, the limitations for these fuels would be the same as those discussed in earlier chapters for the specific fuels/technologies.

9.4 **Environmental and Other Considerations**

Algae production can have impacts on a number of different environmental areas, including water, land, soil, biodiversity, and air (NRDC, 2009). These areas need to be examined as algae production is developed to ensure that there are no unanticipated environmental issues if this technology reaches a commercial level. For cultivation, consideration should be given to the process impacts on water use and discharge and land use and associated infrastructure requirements, and the impacts of genetically modified organisms (GMO) usage on biodiversity and ecosystem health. For harvesting, the management of the output water, potential toxicity of

any chemicals used, and the energy and carbon balance implications of drying or other mechanical operations should be considered. Similarly for extraction, the energy and carbon balance implications of any process will need to be considered, along with the toxicity of any chemical solvents.

The lifecycle GHG emissions for algae-based fuels are another important consideration. CARB has not evaluated the carbon intensity values for algae-based fuels yet as part of its LCFS requirements, but it is anticipated that the algae-based fuels would provide benefits relative to both petroleum diesel and gasoline. If the algae are utilized to produce a biodiesel fuel then NO_x emissions will be an important environmental issue, as discussed in chapter 4 above.

9.5 Ongoing Algae Research

Lipids production research by algae dates back to the 1940's and 1950's. The United States Department of Energy conducted a comprehensive research program into algae research called the Aquatic Species program between 1978 and 1996 (Sheehan et al., 1998). Since the close of the aquatic species program, federal funding for algae fuel has been limited. More recently, there has been increased interest and funding into algae research. This includes private companies as well as new funding efforts at the Federal level. In the private sector, this includes larger companies, such as ExxonMobil, Chevron, and Shell, as well as small venture companies, such as Sapphire Energy, Solazyme, Algenol, Phycal, and Algae Venture Systems. The development of these companies and the early algae research are reviewed above in 8.2. The focus of this chapter is on the more recent government initiatives in algae research and on ongoing fundamental research.

The US DOE and NREL have a number of algae research projects underway. NREL is working with Chevron to identify and develop microalgae strains that can be economically harvested and processed into finished transportation fuels. NREL has also initiated a project with the Colorado Center for Biorefining and Biofuels to develop novel microalgae strains. NREL is working with the US Air Force to develop a cost-effective, algae-based jet fuel. NREL has partnered with the Colorado School of Mines and the Carnegie Institute (Stanford), with support from the DOE, to construct chemically detailed metabolic models, to develop methods for high frequency transformation of green algae, and to perform techno-economic assessments of algal biofuels. NREL is working with the Sandia National Lab and the National Resource Council of Canada to isolate algal strains from a variety of northern marine and freshwater habitats. NREL has also collaborated with Sandia National Laboratories and Israeli and US industrial partners to develop cost-effective algal biofuels, including developing cost-effective processes for producing and harvesting algal biomass using open raceway ponds, developing cost-effective methods for extracting algal oil from biomass, and evaluating economic feasibility for algal biofuels scale-up. In-house NREL programs include assessing lipid production in algae, utilizing high throughput transcriptomics analysis of microbial strains, developing genetic models, evaluating enzymatic disruption of algal cell walls, identifying novel promoters in green algal species, and developing novel cyanobacterial biofuels.

Supported by DOE's recently formed Advanced Research Projects Agency-Energy (ARPA-E), Univenture and Algaeventure Systems jointly received \$5.9 million to develop a new and

inexpensive method for harvesting algae utilizing low energy surface chemistry properties in a mechanical-electrical device. Univenture and Algaeventure Systems (Univenture Inc. and AlgaeVenture Systems, 2009) have developed an innovative algae harvesting, dewatering, and drying method using capillary action to efficiently extract water and harvest algae that reduces energy consumption by more than 90 percent over the previous method, which used energy-intensive centrifuges to extract the water.

In December, 2009, the U.S. DOE announced an award of \$100 Million to three algae biorefineries to accelerate construction of pilot plants and demonstration of the feasibility of biofuel production at commercial scale facilities. The three biorefineries are: an Algenol Biofuels Inc. facility in Freeport, Texas, a Solazyme, Inc. facility in Riverside, Pennsylvania, and a Sapphire Energy, Inc. facility in Columbus, New Mexico. Algenol Biofuels will use its recently developed Direct To Ethanol[®] technology to make ethanol directly from carbon dioxide and seawater using algae. Solazyme will demonstrate an integrated scale-up of its novel heterotrophic algal oil biomanufacturing process. Sapphire Energy has worked with identifying algae strains with desirable characteristics for production of gasoline, jet, and diesel fuel. The goal of this project is to cultivate algae strains with high yields in ponds and convert the algae into jet fuel and diesel, using the Dynamic Fuels' refining process.

In January 2010, U.S. DOE Secretary Chu (Westervelt, 2010; Morello and Pate, 2010) pledged \$78 million dollars in funding for research and development of algae-based fuels. The National Alliance for Advanced Biofuels and Bioproducts (NAABB) will receive \$44 million "to develop 'a systems approach for sustainable commercialization' of algae-based gasoline, diesel and jet fuel." The NAABB is directed by José Olivares with Los Alamos National Laboratory (LANL) in conjunction with the Donald Danforth Plant Science Center (DDPSC). The NAABB partners include the Pacific Northwest National Laboratory, University of Arizona, Brooklyn College, Colorado State University, New Mexico State University, Texas AgriLife Research-Texas A&M University System, University of California Los Angeles, University of California San Diego, University of Washington, Washington University in St. Louis, Washington State University, AXI, Catilin, Diversified Energy, Eldorado Biofuels, Genifuel, HR Biopetroleum, Inventure, Kai BioEnergy, Palmer Labs, Solix Biofuels, Targeted Growth, Terrabon, and UOP. The NAABB consortium will integrate resources from companies, universities, and national laboratories to develop and demonstrate the science and technology of algal production, harvest, extraction, sustainability, and coproducts, that can be implemented at a commercial scale (NAABB Website, 2010). The Donald Danforth Plant Science Center, which was established in 1998 in St. Louis, Missouri, was also awarded \$15 million in 2009 from the DOE's fund for Energy Frontier Research Centers to form the Center for Advanced Biofuels Systems (CABS) to study the conversion of energy captured from photosynthesis in the single cell algae and how it is channeled into oil metabolically. The research focus on identifying catalysts and enzymes that could be engineered into the organism to improve photosynthesis efficiency and oil yields.

The National Advanced Biofuels Consortium, led by NREL and the Pacific Northwest National Laboratory will receive \$33.8 million "to develop biomass-based hydrocarbon fuels that can work within the existing refining and distribution infrastructure (Westervelt, 2010)." The article notes that despite the DOE showing a preference for algae that, "By even the most optimistic of

predictions, however, actually producing fuel from algae at scale and at a cost that is palatable to consumers is a good 10 years away.”

In July 2010, DOE invested another \$24 million to three research groups, consisting of partners from academia, national labs and private industry, to overcome the obstacles of commercialization of algae-based biofuels. The three consortia are the Sustainable Algal Biofuels Consortium (Mesa, Arizona) led by Arizona State University, the Consortium for Algal Biofuels Commercialization (San Diego, California) led by the University of California, San Diego, and the Cellana, LLC Consortium (Kailua-Kona, Hawaii): led by Cellana (a joint venture between Shell and HR BioPetroleum). The Sustainable Algal Biofuels Consortium will investigate biochemical conversion of algae to fuels and products, and analyze physical chemistry properties of algal fuels and fuel. The Consortium for Algal Biofuels Commercialization will focus on algal fuel feedstock development, mainly on new approaches for algal crop protection, algal nutrient utilization and recycling, and developing genetic tools. The Cellana, LLC Consortium will evaluate new algal harvesting technologies integrated with pilot-scale cultivation test beds, and develop microalgae grown in seawater as animal feed.

Scientists at NASA have recently developed a novel algae photo-bioreactor, which is an Offshore Membrane Enclosure for Growing Algae (OMEGA) in municipal wastewater to produce biofuel and various other products (NASA News, 2009). The OMEGA algae bioreactors are plastic bags with forward-osmosis membranes that can grow fresh water algae using the nutrients in the sewage. The algae in the plastic bags, floating in the ocean, absorbs sunlight and carbon dioxide through the membrane to produce lipids for fuels, meanwhile it cleans the wastewater. The clean fresh water and oxygen is then released to the ocean through osmosis membranes. Growing algae in OMEGA does not require fresh water, land, or fertilizer. Funded by NASA’s Aeronautics Research Mission Directorate and the California Energy Commission, a demonstration project is planned to evaluate the feasibility and scalability of OMEGA in terms of biology, engineering, environmental and economics. It is predicted that algae cultivated in the OMEGA system could produce approximately 21 billion gallons biofuel a year, enough to supply U.S. aviation fuel demands.

Fundamental Research

There are a number of fundamental research programs in algal biofuel at universities and in the private sector. This subsection provides a summary snapshot of some of this research. The research programs discussed below were primarily from an Algal biofuels Symposium that was conducted by the San Diego Center for Algae Biotechnology in April of 2010.

- Researchers from Michigan State University have been studying the accumulation of triacylglycerols (TAGS) and the formation of lipid droplets during nitrogen deprivation for model green algae *Chlamydomonas reinhardtii* (Benning, 2010). They have used genome annotation to outline the metabolic network involved in lipid biosynthesis, enabling the identification of key enzymes for TAGS biosynthesis, fatty acid modification and lipid degradation.
- Researchers at Washington University in St. Louis have evaluated the production of lipid bodies (LB) for the starch blocked biosynthesis under various growth conditions

(Goodenough, 2010). Understanding the yields of the lipid bodies (LB) is one of the keys to increased algae production capacity is, so it is important to understand how these yields can change under different growth conditions.

- Cyanobacteria have a number of desirable characteristics in production strains, but previously the harvesting of polar lipids has been a barrier to successful use of membrane-rich cyanobacteria. Since new technologies are emerging for harvesting polar lipids, however, the promise of membrane-rich cyanobacteria for alternative fuel production is currently being re-examined by researchers at the University of California at San Diego (Golden, 2010).
- Researchers at the Carnegie Institute for Science in Stanford, CA have studied the potential for algae to meet transportation diesel fuel needs (Grossman, 2010). They concluded that only about 20% of the demand for diesel can be met from algae.
- Researchers at Rutgers University have been developing more systematic, hypothesis-driven methods for developing algal strains (Falkowski, 2010). They suggest using an “input/output” biophysical approach, in which the unit of product (e.g., lipid) is related to light absorbed, to optimize yield strategies with practical applications.
- Scientists with the Biorefining and Carbon Recycling Program at the University of Georgia have been investigating methods to produce algae utilizing industrial, agricultural, aquaculture and municipal wastewaters, and livestock industry wastes, such as poultry litter. Preliminary research results showed that phosphorous in the waste water, which is a nutrient for algae, can be effectively removed by some algae strains (Chinnasamy, 2009).
- Funded by the DOE, researchers at Montana State University and Utah State University have been evaluating the oil contents of different algae cultures to identify optimal algae types with high oil production rates (Becker, 2008). The best candidate algae will be grown in larger numbers at Utah State University in a 10,000 gallon "raceway" bioreactor to test the oil content the algae on a larger scale.

9.6 Recommendations for Algae Research

Because algae has a number of advantages, relative to biofuels from terrestrial sources, interest and investment in algae-based fuels is rapidly growing. Considerable research is still needed to make algae-based fuels a viable transportation substitute, however. The increase in funding at the Federal Level and the number of companies becoming involved in the study and development of algae-based fuels is one important indicator of the optimism behind algae-based fuels. Using optimistic estimates, however, it is likely that economically commercial production of algae-based fuels is at least 10 years away (Westervelt, 2010). Algae-based fuels could, however, represent the next generation of fuels that would follow those derived from cellulosic ethanol.

It is clear that before algae-to-biofuel production sees widespread commercialization there is significant research and development that still needs to be done. Although the process of making biofuels from algae is already known and proven, there are obstacles that need to be overcome before the process can be implemented on a commercial scale. A primary challenge facing biofuels production from algae is economic. Research is underway to identify the most appropriate strains. Work also continues on refining methods for extracting and processing the oils. Some of the main areas of current investigation include:

- Faster growth, higher biological efficiency.
- Improved large-scale culture stability, including improved culture consistency, resilience, community stability, and resistance to predators present in a given environment.
- Wider ambient growing conditions.
- Higher percent of total biomass as oil.
- Reduced water and nutrient requirements
- Basic research in multi-trophic⁴, molecular-level algal ecology
- Improved oil extraction and fractionation technology
- Use of algal remnants after the lipids or other desirable fuel precursors have been extracted
- Lifecycle analysis of energy and carbon in selecting preferred fuel conversion technologies
- Integration issues and opportunities for algal cultivation facilities co-located with industrial CO₂ sources and/or wastewater treatment facilities
- Evaluation of economies of scale vs. advantages of decentralized production considering parasitic losses of CO₂ transport.

Although funding for algae fuel declined after the close of the Aquatic Species program until recently, nevertheless, strides have been made in genomic and proteomic methods that can be utilized to understand the mechanism involved in algae production. The DOE organized a workshop in December of 2008 to develop a roadmap to guide research in Algal biofuels technology (DOE, 2009f). Some of the key areas emphasized in this roadmap are summarized below since this provides a context for understanding the framework of research funding at the Federal level and how California might be able to augment these efforts in an effective manner.

The workshop and associated roadmap addressed the following main topic areas/technical barriers:

- Algal biology
- Feedstock Cultivation
- Harvest and Dewatering
- Extraction and Fractionation of Microalgae
- Algal Biofuel Conversion Technologies
- Co-Products
- Distribution and Utilization of Algal Based-Fuels
- Resources and Siting
- Corresponding Standards, Regulation and Policy
- Systems and Techno-Economic Analysis of Algal biofuel Deployment

⁴ **Integrated Multi-Trophic Aquaculture (IMTA)** is a practice in which the by-products (wastes) from one species are recycled to become inputs (fertilizers, food) for another.

- Public-Private Partnerships

One of the most critical areas of research is in the development and optimization of algae strains. This includes strains with fast growth rates and high efficiency, improved strain robustness, resistance to predator and pathogen attack, the production of higher levels of oils or lipids, and ability to grow under a wider range of environmental conditions including wider temperature ranges, and reduced water and nutrient requirements. Optimizing strains of heterotrophic algae that are grown in the dark, would also allow for greater diversity in the conditions that could be used for algae for fuel production. Identification of species that can better utilize shorter wavelengths to grow would also improve cultivation, since algae growth rates are often limited by light penetration into the ponds, and shorter wavelengths have greater penetration depths (Hannon, et al., 2010). Other algae species that process nutrients efficiently, but do not produce the desired concentrations of oils and lipids, may have waste products that can be efficiently converted to oils and lipids by other species. One aspect of strain optimization is the isolation, selection and screening of strains. The development of high volume methods for screening multiple phenotypes for characteristics such as growth rates and metabolite productivities could facilitate this process. Understanding the fundamental pathways of microalgae growth is important. This includes understanding the regulation and synthesis of fatty acids and triacylglycerols, which are the main storage compounds in algae, the photosynthetic regulation of lipid synthesis, and the partitioning of carbon between lipids and alternative storage products, such as starch, and the pathways for such synthesis. The methods used to understand these different aspects include genomics, transcriptomics, proteomics, metabolomics, lipidomics, algal model systems, systems biology, and metabolic engineering. There was also some interest in developing algae strains that could directly produce hydrogen.

The cultivation of algae is a key area where further development is needed. The DOE roadmap included provisions for both open and closed pond systems, although it was suggested that an open source test bed for R&D could be useful for research in this area. The stability of large scale cultures, nutrient sustainability and management, and water management were all issues identified in the DOE roadmap. To better control culture stability, it was suggested that automated biological and chemical monitoring would be useful for understanding the health and composition of the pond, early identification of invasive species, predators, and pathogens, and the chemical treatment of the pond. It will also be important to understand the pond speciation, ecology dynamics, and frequency of contamination events. Nutrient supply issues can have a sizeable impact on cost, sustainability, and production siting. Issues related to this include controlling the nutrient levels, finding inexpensive sources of nutrients, and looking for opportunities to recycle nutrients. The most critical nutrients for evaluation include nitrogen, phosphorous, iron, and silicon. Water management represents one of the largest issues for algal biofuels, with enormous water demands for large cultivation systems. Important areas of emphasis in water management include addressing changes in water quality due to evaporation; developing designs that can conserve water, optimizing and controlling water recycle, and water treatment for entering and exiting water.

The downstream processing of the algae includes harvesting, dewatering, extraction, fractionation, and final processing into a useable transportation fuel. The DOE roadmap document reviews a number of techniques for extraction/fractionation. These included co-solvent

or two solvent systems, mechanical disruption and cell rupture, subcritical water extraction, accelerated solvent extraction, supercritical methanol or CO₂, and milking. The roadmap established several performance goals for extraction including a 1st generation process with a 75% recovery of algae and an nth generation process with a 90% recovery of algae. The technologies for extracting algae are expensive, however, in terms of either equipment costs or energy requirements (Hannon, et al., 2010). Systems or engineering improvements in these areas would improve the economic viability of algae production as a whole. This could include the development of multitasking extraction processes or improved methods for dealing with water in the downstream processes. Studying and understanding the fundamental aspects of algae relating to downstream processing could also be valuable. This could include understanding processing impacts on cell wall composition and understanding lipid genesis, composition, and structure. The production of fuels from algae is most typically done by processing the algae extracts using transesterification, biochemical catalysis, chemical catalysis, supercritical processing, or even using petroleum processing. The algae can also be processed as a whole using pyrolysis, gasification, or anaerobic digestion. Certain algae can also be processed directly into biofuels such as alcohols, alkanes, or hydrogen. One additional consideration in processing algae is the types of co-products that are also made during this processing that can contribute to the overall economics. This could include products such as food supplements, fatty acids, antioxidants, coloring agents, fertilizers, and other specialty products.

10 Natural Gas and LPG Fuel Pathways

10.1 Introduction

Engines can be designed to run on gaseous fuels. Gaseous fuels have a lower energy density compared to liquid fuels and therefore, for the same quantity of fuel, the range of travel is shorter. There is also a more limited vehicle and refueling infrastructure for gaseous fuels. It is generally believed that gaseous fuels can produce less smog causing emissions and toxic pollutants, however. This makes these desirable alternative fuels, especially in densely populated areas. Gaseous fuels that have been and are being used include natural gas (NG) and liquefied propane gas (LPG). Since these fuels are similar in terms of their gaseous nature and utilization, they are discussed together in this chapter.

10.2 Natural Gas

10.2.1 *Development of Natural Gas for Transportation Applications*

10.2.1.1 Feedstocks for Natural Gas

NG is typically produced along with crude oil or from deep natural gas wells. Navigant Consulting (2008) estimated that the total domestic proved reserves plus the ultimately recoverable domestic resource base is in the range of 1,680 to 2,247 Tcf. The estimates include reserves in crude oil, deep natural gas wells, and natural gas in tight sands, coal beds, and shale. At current production levels, this is enough gas for 88 to 117 years. NG produced from fossil fuel is non-renewable, however, and hence is not a primary focus of this research roadmap.

Biomass can be a renewable source of NG. Anaerobic digestion of organic waste material in landfills produces a methane-rich gas that is commonly called Biomethane. Organic waste includes manure, crop residues, food processing waste, slaughterhouse waste, rendering plant wastewater, and green waste from municipal/commercial collection programs. Landfill gas contains significant amounts of CO₂ and hydrogen sulfide, however, which would have to be substantially reduced to be used in motor vehicles.

Krich et al. (2005) estimate the total gross potential production of biomethane in California is about 124 billion ft³ CH₄/yr (BCF/yr), but that due to inefficiencies in collection, contamination with other wastes, and other uses, the technical potential (i.e., the amount that can realistically be collected and used) is 23 BCF/yr. Over half of the total gross potential of 124 BCF/yr is from processed green waste and landfills. Of the technical potential, dairy manures represent about 2/3 of the 23 BCF/yr.

The California Biomass Collaborative (2008) estimated that potential landfill gas production exceeds 118 BCF/yr with a potential recovery of 79 BCF/yr. In 2003, there were 330 active landfills in California and 217 landfills had existing or potential landfill gas to energy recovery systems (See Table 3.4.1 in (California Biomass Collaborative, 2008)). Currently, this recovered biomethane is primarily used to generate electricity or heat. The report also states that biogas from waste treatment plants adds 16 – 18 BCF/yr.

10.2.1.2 Production of Natural Gas

While the major production of natural gas is from deep natural gas wells, there are several other minor sources that are fossil fuel-based. These sources include coal beds, low permeability shale beds, blast furnace gas, coke-oven gas, manufactured gas (from destructive distillation of coal or the thermal decomposition of oil), refinery gas, and synthetic natural gas (from conversion or reforming of petroleum hydrocarbons) (USEIA, 2010a).

Anaerobic digestion is another method for the production of NG from biomass. Anaerobic digestion is a fermentation process whereby anaerobic bacteria breakdown biogenic organic matter in the absence of oxygen into a biogas containing mostly methane and carbon dioxide. Anaerobic digestion is the primary decomposition process occurring in landfills. It is employed in many wastewater treatment facilities for sludge degradation and stabilization. It can also be used in dairies and animal feeding operations to mitigate the environmental impacts of manure lagoons with some capture of methane for energy production.

The two main types of anaerobic digester systems are based on a single reactor stage or multiple reactors. In single stage systems, the essential reactions occur simultaneously in a single vessel. With 2-stage or multi-stage reactors, the reactions take place sequentially in at least two reactors. Single stage systems are generally simpler to operate, have fewer components for maintenance or failure, and have smaller capital costs. Multistage systems are more complex, but offer the potential for increased methane production and increased overall biodegradation of the feedstock by separating and optimizing the different steps of the biochemical process.

Anaerobic digestion and aerobic composting is common in Europe, due to more stringent waste management disposal policies. By the end of 2010, it is expected that over 200 plants will be installed in Europe with an installed capacity of 6 million tons/year for the treatment of mixed municipal solid waste and source separated biowaste (De Baere and Mattheeuws, 2010). More than 70 of these plants have been installed in the last 5 years. Single stage reactors represent a majority of these facilities, with two-stage digesters representing less than 10% of the existing market share. Germany, Spain, and France are the European countries with the most installed capacity. Progress in anaerobic digestion of MSW for other countries such as Canada, Australia, Japan, and elsewhere, is summarized in Rapport et al. (2008). These installations are for the most part all using the produced methane as a heating source or for generating electricity.

There is less interest in anaerobic digestion in the US and California. Some California jurisdictions are investigating anaerobic digestion as a potential strategy for landfill diversion. UC Davis has been conducting research in anaerobic digestions for several decades. Anaerobic digestors have also been installed or planned for Folsom prison, Stanton, Los Angeles, and Lancaster, CA. A review of these activities is provided in Rapport et al. (2008).

Biogas and landfill gas derived from renewable sources can be liquefied to provide “renewable liquefied natural gas (LNG)”. Part of this process would remove most of the non-methane components of the gas such as CO₂, H₂S, H₂O and various contaminants. Waste Management and Linde have developed a biomethane facility at the Altamont Landfill that began operation in November of 2009 (CalNGV News, 2010). This \$15.5 million facility is designed to produce

13,000 gallons a day and is the largest facility of its kind in the world. Waste Management is currently looking for a location to put a similar facility in Southern California.

10.2.2 *Natural Gas Distribution and Utilization*

NG has been utilized in vehicle applications for over 30 years at various levels. The development of specifically designed natural gas vehicles (NGVs) and the associated infrastructure has been primarily driven by regulatory and other incentives, because natural gas is generally considered to be a cleaner fuel than gasoline or diesel. While NG engines and refueling stations are available, the infrastructure for NG vehicles is still relatively limited in comparison with comparable petroleum-based fuels or liquid fuels that can more readily be adapted to the conventional petroleum infrastructure. The limitations of the NG infrastructure and vehicle availability, hence, represent some of the most critical roadblocks in the distribution and utilization of NG in transportation applications.

Due to its gaseous nature and relatively low energy density on a volumetric basis, NGVs have a number of disadvantages for vehicle applications. NGVs typically run from compressed natural gas (CNG) and have a more limited range and larger fuel tanks due to its lower energy density. The retail price of the vehicles is also higher than that of a comparable gasoline-powered vehicle. There are some cost advantages of NGVs, however, such as lower fuel costs and State and Federal incentives. The primary market for NGVs has been cities and companies rather than the general public. The Gas Technology Institute (GTI) estimated the total number of NGVs in California, based on information from various studies, ranged from 17,800 to 29,765, with light-duty representing 11,300 to 21,000 vehicles (Liss 2006). While a number of manufacturers have made NG gas vehicles in the past, Honda (with its Civic model) is currently the only manufacturer producing dedicated OEM NG vehicles. A number of certified retrofits for NG use in LDVs are available, however, including BAF technologies with a number of certified retrofits for Ford vehicles and Baytech Corporation with retrofits for General Motors (GM) vehicles.

Another limitation of NGVs is that the infrastructure for NGVs is not nearly as developed as it is for corresponding petroleum-fueled vehicles. According to the Natural Gas Vehicles for America association, there are approximately 1,100 NG stations throughout the country (Yborra 2007) compared to 200,000 gasoline filling stations. By the end of 2009, 202 CNG and 27 LNG stations were located in California, which has the most NG stations of any state in the US.

10.2.3 *Technical Limitations of Natural Gas as a Transportation Fuel*

10.2.3.1 Technical Limitations for Natural Gas Feedstocks

While there is a significant supply of NG from fossil fuel sources, this NG is nonrenewable and hence does not address many of the primary objectives of developing alternative fuels. Organic waste materials are an alternative source of NG production through anaerobic digestion, but this material is currently used primarily for the generation of electricity and heat. NG can also be produced via thermochemical processes. In this case, the range of feedstocks would include a broader range of feedstocks, with similar limitations to those discussed above.

10.2.3.2 Technical Limitations for Natural Gas Production

The primary unique production technology for biomass-based NG would be anaerobic digestion. While there is a potential to expand anaerobic digestion, the level to which this production route can be expanded will be limited by collection inefficiencies, contamination, and the potential to use the biomethane produced for electricity or heat. Additionally, the natural gas produced from sources such as landfills will contain impurities, such as CO₂ and hydrogen sulfide, which would have to be removed in order to meet the quality specifications for transportation fuels.

10.2.3.3 Technical Limitations for Natural Gas Distribution and Utilization

The potential of NG as a transportation fuel is significantly limited by both the distribution infrastructure and vehicle availability constraints. Given that only 229 NG stations are available in California, a significant investment in infrastructure would be needed before these fuels could be expanded to widespread use in the consumer fleet. The availability of NGVs is also relatively limited, and there is not a significant interest by automobile or engine manufacturers in making NG the primary alternative fuel for the future. Other limitations for NG in vehicles include reduced energy density and corresponding constraints in storage and range.

10.2.4 *Environmental Considerations for NG*

CARB (2009a) has evaluated the Well to Wheel (WTW) GHG emissions for various scenarios for CNG and LNG using the CA-GREET model. These results are provided in Table 11-1. The results show that for nearly all examined scenarios, CNG and LNG provide lower carbon intensity values than either gasoline or diesel. The magnitude to the carbon intensity reductions depends on a number of factors including whether the feedstock is renewable or not and where it comes from, how the fuel is produced, how the fuel is transported, and other factors in the utilization of the fuel, such as compression. The production of CNG or LNG from renewable fuels has a very low carbon intensity that represents over an 80% reduction compared to conventional fuels, and is less than electricity or hydrogen.

Table 10-1: Adjusted Carbon Intensity Values for CNG and LNG.

Fuel	Pathway Description	Carbon Intensity Values (gCO ₂ e/MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Gasoline	CARBOB – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	95.86	0	95.86
Diesel	ULSD – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	94.71	0	94.71
Compressed Natural Gas	California NG via pipeline; compressed in CA	67.70	0	75.22
	North American NG delivered via pipeline; compressed in CA	68.00	0	75.56
	Landfill gas (bio-methane) cleaned up to pipeline quality NG; compressed in CA	11.26	0	12.51
	Dairy Digester Biogas to CNG	13.45	0	14.94
Liquefied Natural Gas	North American NG delivered via pipeline; liquefied in CA using liquefaction with 80% efficiency	83.13	0	92.37
	North American NG delivered via pipeline; liquefied in CA using liquefaction with 90% efficiency	72.38	0	80.42
	Overseas-sourced LNG delivered as LNG to Baja; re-gasified then re-liquefied in CA using liquefaction with 80% efficiency	93.37	0	103.74
	Overseas-sourced LNG delivered as LNG to CA; re-gasified then re-liquefied in CA using liquefaction with 90% efficiency	82.62	0	91.80
	Overseas-sourced LNG delivered as LNG to CA; no re-gasification or re-liquefaction in CA	77.50	0	86.11
	Landfill Gas (bio-methane) to LNG liquefied in CA using liquefaction with 80% efficiency	26.31	0	29.23
	Landfill Gas (bio-methane) to LNG liquefied in CA using liquefaction with 90% efficiency	15.56	0	17.29
	Dairy Digester Biogas to LNG liquefied in CA using liquefaction with 80% efficiency	28.53	0	31.70
	Dairy Digester Biogas to LNG liquefied in CA using liquefaction with 90% efficiency	17.78	0	19.76

One of the primary espoused benefits of gaseous fuels such as CNG and LNG are that they provide reductions in vehicle emissions. While this is true in an ideal sense, there have been significant advances in the emissions control technologies for both gasoline and diesel vehicles. Emissions from advanced gasoline vehicles meeting today’s most stringent regulations are significantly lower than those of past vehicles, and in some cases near the detection limits of existing emissions measurement methods. As of 2010, diesel vehicles are also being equipped with diesel particulate filters and either NO_x aftertreatment or changes in engine control strategies that control emissions to very low levels. Additionally, in some cases, it has been found that alternative fuel vehicles can have higher emissions than a corresponding gasoline or diesel vehicle if they are malfunctioning. Such high emissions from alternative fueled vehicles have been observed in a number of studies over the past two decades. Overall, given the advances in gasoline and diesel vehicle technology, it is likely that any emissions benefits from CNG or LPG would be minimal past the near term.

10.2.5 *Ongoing Research in Anaerobic Digestion for NG production*

Anaerobic digestion (AD) is a fermentation process whereby anaerobic bacteria breakdown biogenic organic matter in the absence of oxygen into a biogas containing mostly methane and carbon dioxide. It is the primary decomposition process occurring in landfills, and it is also used in wastewater treatment facilities, and with dairies and animal feeding operations. The technology is well developed in Europe, where over 200 AD facilities for the treatment of mixed municipal solid waste and source separated biowaste are currently in place (De Baere and Mattheeuws, 2010). These installations are for the most part all using the produced methane as a heating source or for generating electricity, however. A major limitation of the AD technology is that the biogas produced is a very poor quality for transportation fuel production. Specifically, the methane content of biogas produced from anaerobic digestion sources is low, and can range from approximately 35-70% (Persson et al., 2006). Current motor vehicle CNG specifications, on the other hand, require a methane content of 88 mole % min and limit inert gases to 1.5-4.5 mole% max (Durbin and Miller, 2009b). Thus, significant processing would be required to upgrade anaerobic biogas into a gas that would meet transportation specifications.

AD systems come with single-stage reactors or multiple stage reactors, and can be operated wet or dry. A review of AD technologies is given in Rapport et al. (2008), and their conclusions are summarized here. In Europe, the AD technology has progressed substantially in the last 10 years, with expansion fueled by waste management policies. Experience is more lacking with the AD technology in the US, but technology development/implementation would be facilitated by the efforts in Europe. It is not clear which technology will be the most effective going into the future. There are several research groups in the U.S. that are actively involved in adapting and improving existing MSW AD systems. Single-stage AD systems are the most prominent in Europe. Other new digester designs such as sequential and phased batch and two-stage digesters are currently being tested in the lab as well as in the marketplace.

10.2.6 *Recommendations for Biomethane/CNG*

The development of CNG/LNG as a transportation fuel will be limited by both vehicle availability and infrastructure for delivery to retail stations. CNG has been developed primarily for fleet applications in California and there are OEM technologies for both light-duty vehicles and heavy-duty engines. While some improvements in vehicle and engine technology for CNG could be made, it is not likely that additional PIER research would lead to significant breakthroughs that would facilitate wide spread commercialization of these technologies.

Although anaerobic digestion is a potential source of methane that could be used in transportation applications, the produced biomethane will likely continue to be used for generation of heat and/or electricity since it would be uneconomical to upgrade to produce a transportation quality fuel.

In summary, we do not recommend investing PIER dollars towards the development of CNG or biomethane for transportation uses.

10.3 Propane/LPG

10.3.1 Development of LPG as a Transportation Fuel

10.3.1.1 LPG Feedstocks

Currently, propane, the primary component of LPG, is produced from fossil fuels, with the majority of California production a by-product of refining operations. By choosing an appropriate production method, however, nearly any biomass source is a potential propane feedstock.

10.3.1.2 LPG Production

Methods for producing propane from biological sources are in their infancy, and are largely at research stage. Production methods that have been discussed in the literature include: converting glycerin to propane (Osava, 2008), (Cetane Energy, LLC, 2010), (Kittrell, 2007), (Kittrell, 2008), fermentation of the sugars found in corn or sugarcane (Bourzac, 2007), heterogeneous catalytic cracking of acyl glycerides (the main components of vegetable oils and animal fats) (White, et. al, 2007), and conversion of the oxygenates derived from biomass gasification over acidic ZSM-5 catalyst at temperatures of 400°C (Daggolu et al., 2007).

10.3.1.3 Propane Utilization and Distribution

Since propane can be liquefied at relatively low pressures, sufficient volumes of it can be stored in containers to provide a reasonable travel distance for use in vehicles. LPG does yield a somewhat reduced driving range, however, because it contains only about 70-75% of the energy content of gasoline, but fleet owners find that propane costs are typically 5% to 30% less than gasoline (PERC, 2010).

According to the Propane Education and Research Council (PERC, 2010) propane is the third most common engine fuel today, after gasoline and diesel. They also state that “it comes with an existing and affordable refueling infrastructure”. While this statement is true for the primary vehicles using this fuel, namely forklifts, fleets operating within a limited range, and some off road vehicles, it is not true for general transportation usage. The US Energy Information Agency reports (USEIA, 2010b), as of 2008, that only 8,882 LPG vehicles were available in California. Of these ~78% were owned by either private businesses or municipal fleets, with most of the rest of the vehicles being owned by either state agencies or propane fuel providers. There are no light-duty propane vehicles available from automotive OEMs, although there are a limited number of certified retrofit kits (NREL, 2009). The average cost of conversion of a light-duty vehicle from gasoline to dedicated propane fuel ranges from \$4,000 to \$12,000.

Infrastructure is another important issue that would limit LPG expansion. Information from the Alternative Fuels and Advanced Vehicles Data Center (AFAVDC, 2010) indicates that there are 214 stations for LPG vehicles in California and a total of 2,403 stations in the US. Logistically, LPG is shipped from its point of production to bulk distribution terminals via a variety of methods, including pipeline, railroad, barge, truck, or tanker ship. Propane dealers fill trucks at the terminals and distribute propane to end users, including retail fueling stations.

10.3.2 *Technical Limitations of LPG as a Transportation Fuel*

10.3.2.1 Technical Limitations for LPG Feedstocks

The majority of LPG is produced as a byproduct of refining operations, which is essentially tied to the availability of crude oil for refining. The primary limitation of current production is that crude oil is not a renewable feedstock. If methods for converting biomass feedstocks to propane are commercialized, then the primary limitation for this production route will be the availability of the feedstock because of competing uses for generating other alternative fuels.

10.3.2.2 Technical Limitations for LPG Production

Production of propane by refineries is a well developed process with no technical limitations. The primary limitation of this type of production is that the feedstock is nonrenewable. The methods for production of propane from biomass are not sufficiently developed to be economically competitive with current production methods.

10.3.2.3 Technical Limitations for LPG/Propane Distribution and Utilization

Similar to NG, the potential of LPG as a transportation fuel is significantly limited by both infrastructure and vehicle availability constraints. The necessary vehicle technologies and infrastructure for LPG are, in fact, less well developed than NG. At present, light-duty LPG vehicles can only be obtained using a gasoline to LPG retrofit kit and there are no OEM vehicles currently in production. The number of refueling stations in California is very limited, with 214 stations, which is slightly less, but similar to the number of stations for NG vehicles. Additionally, there does not appear to be any driving force for the expansion or continued development of LPG vehicles at the level needed for even small scale commercialization.

10.3.3 *Environmental Considerations for LPG*

Unlike some of the gaseous fuels such as CNG and hydrogen, CARB has not yet evaluated the Well to Wheel (WTW) GHG emissions of LPG. In considering tailpipe emissions it is again worth noting that although gaseous fuel are often perceived to provide lower emissions compared to similar gasoline or diesel engines, this is often not the case, and it should also be noted that even the potential reductions in tailpipe emissions would likely diminish over time as advances in gasoline and diesel technology have already brought tailpipe emissions of the newest vehicles to very low levels.

10.3.4 *Ongoing Research*

A number of methods are available for producing propane or LPG from biomass sources, such as gasification, but the development of methods specifically for the production of propane or optimized for propane is still in its infancy. Methods which have been discussed in the literature include: converting glycerin to propane (Osava, 2008), (Cetane Energy, LLC., 2010), (Kittrell 2007, 2008), fermentation of the sugars found in corn or sugarcane (Bourzac, 2007), heterogeneous catalytic cracking of acyl glycerides (the main components of vegetable oils and

animal fats) (White and Hernandez, 2007), and conversion of the oxygenates derived from biomass gasification over acidic ZSM-5 catalyst at temperatures of 400°C (Daggolu, et al., 2007). It should be noted that, for the latter two references, generally gasoline and diesel range components are the major products rather than propane.

The conversion of glycerin to propane by catalytic hydrogenation could be important in the near term since it would add value to a byproduct of the biodiesel production process. Additional research to optimize the catalyst formulations for this process is currently being pursued (Kittrell, 2008). However, in the long term, it is likely that the expansion of biodiesel production will be limited by feedstock constraints. Thus, at some point, there will no longer be a glut of glycerin and therefore no need to convert glycerin to propane.

The conversion of cellulosic feedstocks to propane by fermentation of the sugars would meet the EISA definition of an advanced biofuel. However, as noted in previous chapters, there are other processes which convert cellulosic feedstocks to gasoline and diesel range hydrocarbons as well. The viability of fermentation for propane production would depend on the favorability of the economics relative to these other technologies.

10.3.5 *Recommendations for LPG*

LPG vehicles are limited by both vehicle availability and infrastructure for delivery to retail stations, similar to CNG. Vehicle technologies for LPG are available, but these technologies are not being supported by the OEMs at the same level as the CNG vehicles. While some improvements in vehicle and engine technology for LPG could be made, it is not likely that additional PIER research would lead to significant breakthroughs that would facilitate wide spread commercialization of these technologies.

While research into some of the production techniques, such as those being studied by White and Hernandez (2007) and Daggolu et al. (2007) could be of value, these techniques would likely be better for optimizing diesel and gasoline production instead of propane, since the infrastructure for delivery of these products exists. Because other methods of producing gasoline and diesel range components from biomass are likely to be more economically attractive, it is recommended that this research should be supported by federal money, as opposed to PIER money.

In summary, we do not recommend the allocation of PIER funding towards research to develop LPG for transportation uses.

11 Hydrogen

11.1 Introduction

Hydrogen is an alternative fuel that could play a bigger role in meeting long-term, future transportation needs. Hydrogen can be produced from fossil fuels, biomass and even by electrolyzing water using renewable solar or wind energy http://www.afdc.energy.gov/afdc/fuels/hydrogen_production.html. There are a number of technical limitations to the development of hydrogen as a transportation fuel. The biggest challenge is to produce hydrogen from renewable biomass sources at a cost that is economically viable. The distribution and utilization of hydrogen is also limited by the cost of hydrogen distribution, the availability of vehicles, and lack of a developed infrastructure. Today, only a limited number of hydrogen fueling stations are available in a few test locations in California to support demonstration projects. Hydrogen vehicles are also severely limited in number, and the vehicle technology is also predominantly in the prototype stages.

This chapter reviews the technical development and ongoing research for hydrogen as a transportation fuel, discusses its technical and environmental limitations and commercialization gaps, and discusses research roadmap funding recommendations for hydrogen.

11.2 Development of Hydrogen as a Transportation Fuel

11.2.1 *Hydrogen Feedstocks*

Natural gas is the predominant feedstock for hydrogen production (DOE, 2006b). Currently, about 95% of the hydrogen used in the U. S. is produced by the steam reforming of methane or other hydrocarbons (DOE, 2006b). Coal, any biomass, and water are other possible feedstocks for hydrogen (DOE, 2006b).

11.2.2 *Hydrogen Production*

Hydrogen can be produced from various resources, such as fossil fuels, biomass, nuclear energy, and water using electrolysis and renewable solar or wind energy. Currently, ~95% of hydrogen used in the US is produced by the steam reforming of natural gas (DOE, 2006b). At high temperatures (700-1100 °C), steam reacts with the methane or other hydrocarbons to produce CO and hydrogen. In a second stage, further hydrogen is produced through the lower temperature (~130 °C) water gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The primary feedstocks for this process are natural gas or other fossil fuels.

Other ways to produce hydrogen, summarized in Table 12-1, include coal and bio-mass gasification, bio-derived renewable liquid reforming, high-temperature thermochemical water-splitting, renewable electrolysis, nuclear high-temperature electrolysis, photobiological process, and photoelectrochemical process. However, most of the technologies for hydrogen production are still at early stages of development. Reports from the FreedomCar and Partnership and the Alternative Fuels & Advanced Vehicle Data Center summarize current hydrogen production technologies and the major challenges to their commercialization (FreedomCar and Partnership 2009a, AFAVDC 2010).

Table 11-1: Summary Table of Hydrogen Production Technologies and their Sources, Benefits, and Challenges.

Hydrogen Production Option	Technology	Feedstock	Energy Source	Benefits	Major Challenges
Distributed Natural Gas Reforming	"Synthesis gas" is created by reacting natural gas with high-temperature steam or by partial oxidation. The synthesis gas is then reacted with water to produce hydrogen.	Natural gas	Natural gas	<ul style="list-style-type: none"> • Most viable approach to begin building hydrogen in near term • Lowest current cost • Existing feedstock infrastructure 	<ul style="list-style-type: none"> • High capital costs • High operation and maintenance cost • Design for manufacturing
Coal And Bio-Mass Gasification	Coal or biomass is converted into gaseous components and then into synthesis gas, which is reacted with steam to produce hydrogen.	Coal, Biomass	Coal, Biomass	<ul style="list-style-type: none"> • Provides low-cost synthetic fuel in addition to hydrogen • Uses abundant and affordable feedstock 	<ul style="list-style-type: none"> • High reactor costs • System efficiency • Feedstock impurities • Carbon capture and storage
Bio-Derived Renewable Liquid Reforming	Renewable liquid fuels such as ethanol are reacted with high-temperature steam to produce hydrogen near the point of end-use.	Biomass	Biomass	<ul style="list-style-type: none"> • Most viable hydrogen pathway in the near term • Existing infrastructure for some feedstocks 	<ul style="list-style-type: none"> • High capital costs • High operation and maintenance costs • Design for manufacturing • Feedstock quantity and quality
High-Temperature Thermochemical Water-Splitting	High temperatures generated by solar concentrators or nuclear reactors drive chemical reactions that split water to produce hydrogen.	Water	Solar, Nuclear	<ul style="list-style-type: none"> • Clean and sustainable • Chemicals are recycled • Only water is consumed 	<ul style="list-style-type: none"> • Cost -effective reactor • Corrosive-resistant material • Immature technology
Renewable Electrolysis	An electric current generated by renewable energy technologies, such as wind or solar, splits water into hydrogen and oxygen.	Water	Wind, Solar	<ul style="list-style-type: none"> • Produce virtually no pollution • Use renewable energy • Use existing electricity infrastructure 	<ul style="list-style-type: none"> • Low system efficiency and high capital costs • Integration with renewable energy sources

Photobiological Process	Microbes such as green algae consume water in the presence of sunlight, producing hydrogen as a byproduct.	Water	Solar	<ul style="list-style-type: none"> • Clean • Highly sustainable 	<ul style="list-style-type: none"> • Identify microorganisms with high solar energy-conversion efficiency • Discover oxygen-tolerant enzymes
Photoelectrochemical Process	Photoelectrochemical systems produce hydrogen from water using special semiconductors and energy from sunlight.	Water	Solar	<ul style="list-style-type: none"> • One-step process • Clean and highly sustainable • Operates at low temperatures 	<ul style="list-style-type: none"> • Develop durable materials with high efficiency • Immature technology

The primary challenge for hydrogen production is cost reduction. The hydrogen cost has to be competitive compared with gasoline in order to enter the light-duty vehicle transportation market. DOE's hydrogen cost goal is to produce and deliver hydrogen at \$3.00-\$4.00/gge (gasoline gallon equivalent) (untaxed) by 2020 based on a 2007 dollar value, independent of the pathway.

Producing hydrogen in a sustainable, cost-competitive manner is the key pathway to a future hydrogen economy. Hydrogen production from solar energy, which is by far the largest renewable energy source, would provide a tremendous opportunity for energy security with a low environmental impact. Technology options for hydrogen production via solar energy currently include solar photovoltaic-based electrolysis, solar photoelectrochemical water splitting, solar biological processes, and solar thermochemical water splitting (FreedomCar and Partnership, 2009b). Table 11-2 lists the options to produce hydrogen from solar energy and the process applications (DOE, 2005b).

Table 11-2: Options of Hydrogen Production via Solar Energy

Options	Distributed Hydrogen Production	Centralized Hydrogen Production
Solar Photovoltaic-based Electrolysis	Yes	Yes
Solar Photoelectrochemical Water Splitting	Yes	Yes
Solar Biological		Yes
Solar Thermochemical Water Splitting		Yes

Photovoltaic-based electrolysis (PV electrolysis) is a process that uses PV devices to capture solar energy to generate electricity and passes the electrical current through water to produce hydrogen. The major hurdle for this technology is the cost of electricity from the solar PV devices (DOE, 2005b). In 2005, electricity produced by PV-based technology cost about \$0.16-0.32/kWh, and the cost of electrolysis produced distributed hydrogen was approximately \$10/gge (gasoline gallon equivalent). Figure 11-1 shows the effect of electricity price on the distributed hydrogen production cost (DOE, 2005). The DOE Solar program has been funding R&D to develop new generations of PV devices to lower the cost of electricity from solar modules. In order to meet DOE's distributed hydrogen price of \$3.00-\$4.00/gge (gasoline gallon equivalent) (untaxed) by 2020, the electricity price needs to be in the range of \$0.04-0.06/kW.

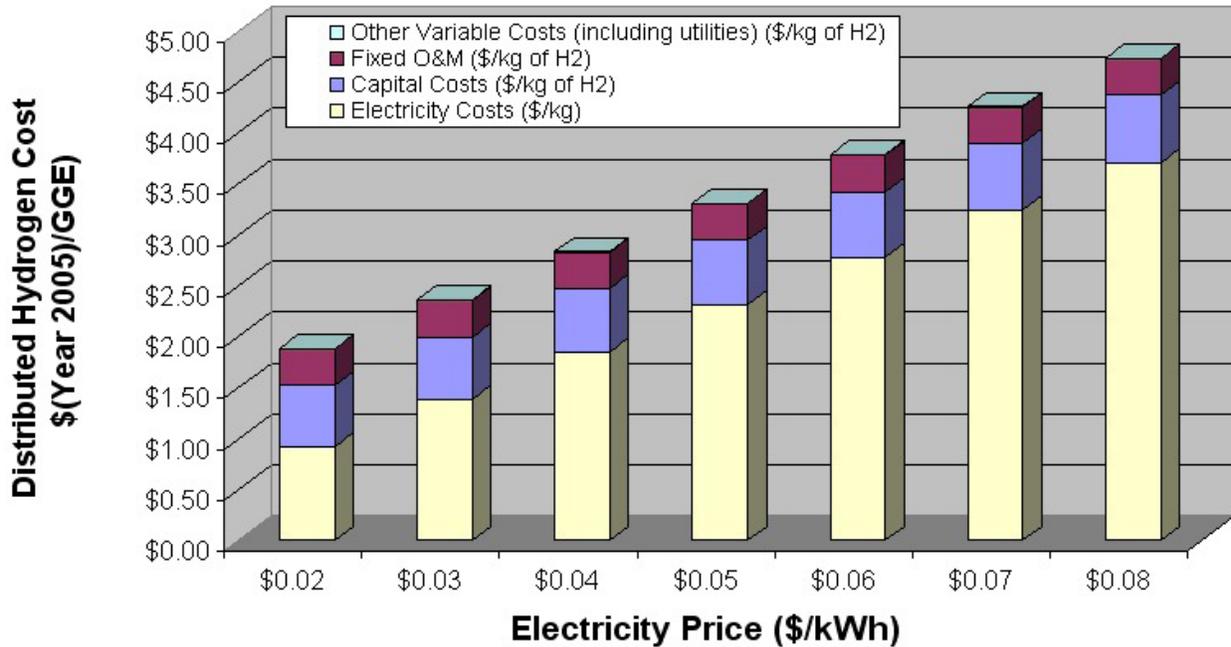


Figure 11-1. Effect Of Electricity Price On The Distributed Hydrogen Production Cost
 (Assumes: 1500 gge/day, electrolyzer at 76% efficiency, and capital cost of \$250/kW)

In the solar photoelectrochemical (PEC) water splitting process, hydrogen is produced from water using sunlight and specialized semiconductors called photoelectrochemical materials (DOE, 2010b). Unlike photovoltaic-based electrolysis, which involves a two-step hydrogen production process, the solar photoelectrochemical splitting process is a one-step process, in which the semiconductor uses solar energy to directly dissociate water molecules into hydrogen and oxygen. The single step PEC water splitting offers the opportunity of improved solar energy conversion efficiency and potentially reduced costs compared to solar PV electrolysis. Three types of PEC reactors, including single PEC slurry-phase reactors, dual slurry-phase reactors, and photoelectrode reactors, can be used in the PEC water splitting process. The three designs for PEC water-splitting systems are illustrated in Figure 11-2, Figure 11-3, and Figure 11-4, respectively. The PEC water splitting process is still in the very early stages of laboratory development. The primary barriers for photoelectrochemical hydrogen production are identifying and developing high-efficiency, durable electrochemical materials that can convert a wide-spectrum of light, designing high-efficiency and corrosion-resistant PEC devices, and integrating the PEC devices to PEC reactor systems (FreedomCar and Partnership, 2009b). A PEC reactor system needs to have the properties of 16% plant solar-to hydrogen (STH) efficiency and 15,000 hours of plant durability to be economically viable for transportation applications (DOE, 2007b). Currently, no single material or system meets both the efficiency and durability target.

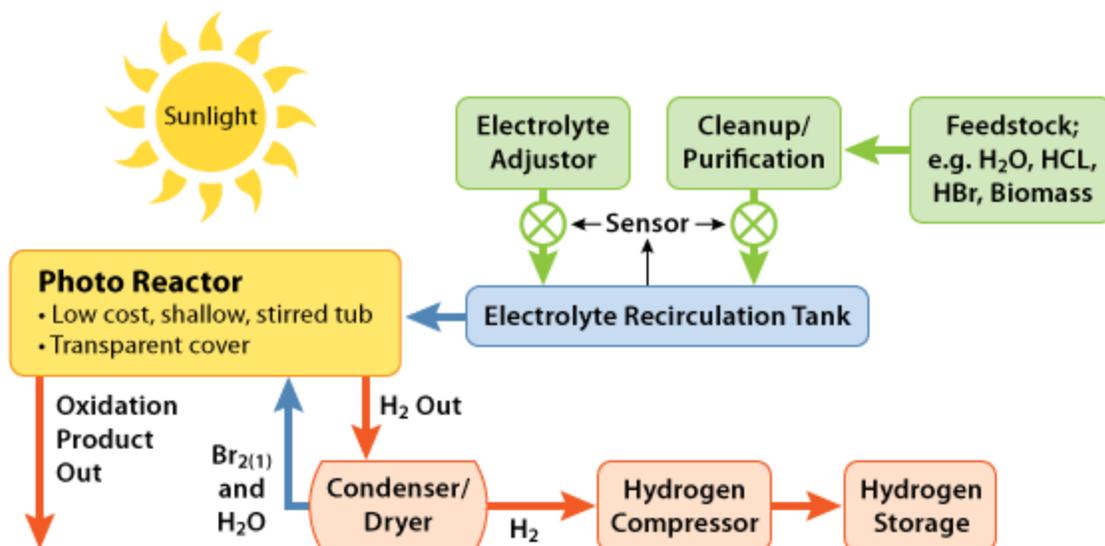


Figure 11-2: Single PEC Slurry-Phase Reactor System for Water Splitting

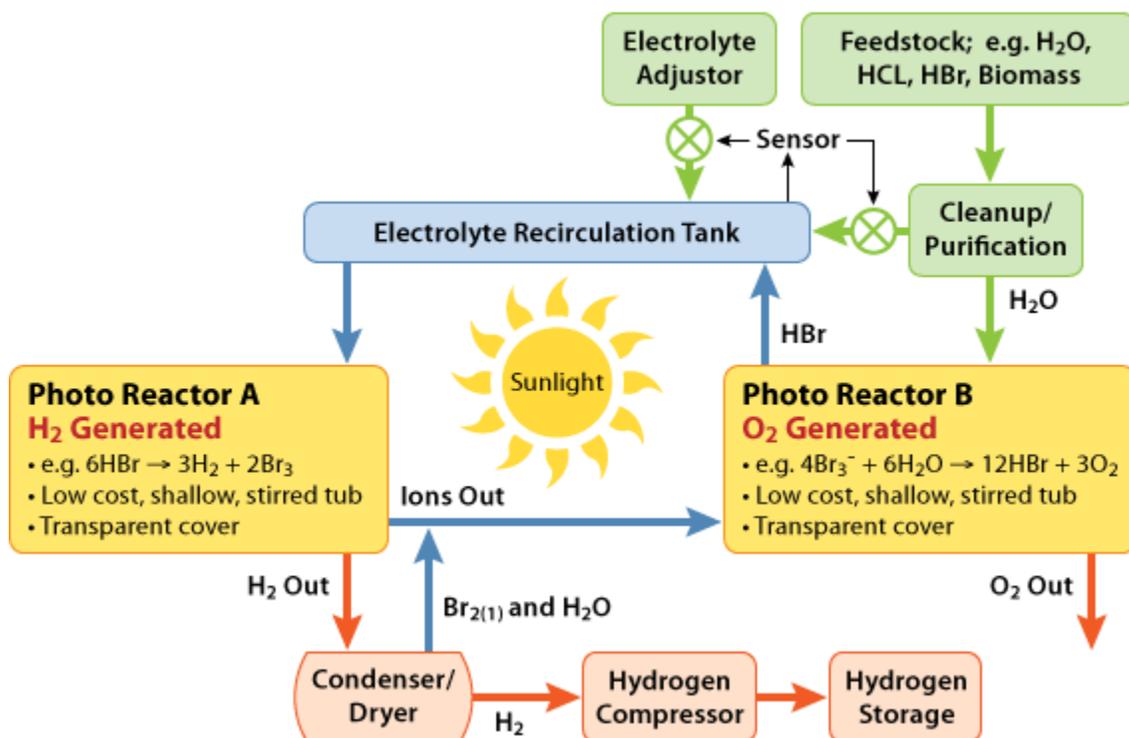


Figure 11-3: Dual Photosystem Slurry-Phase Reactor System for Overall Water Splitting (Br₃⁻ Transfer Ion Example)

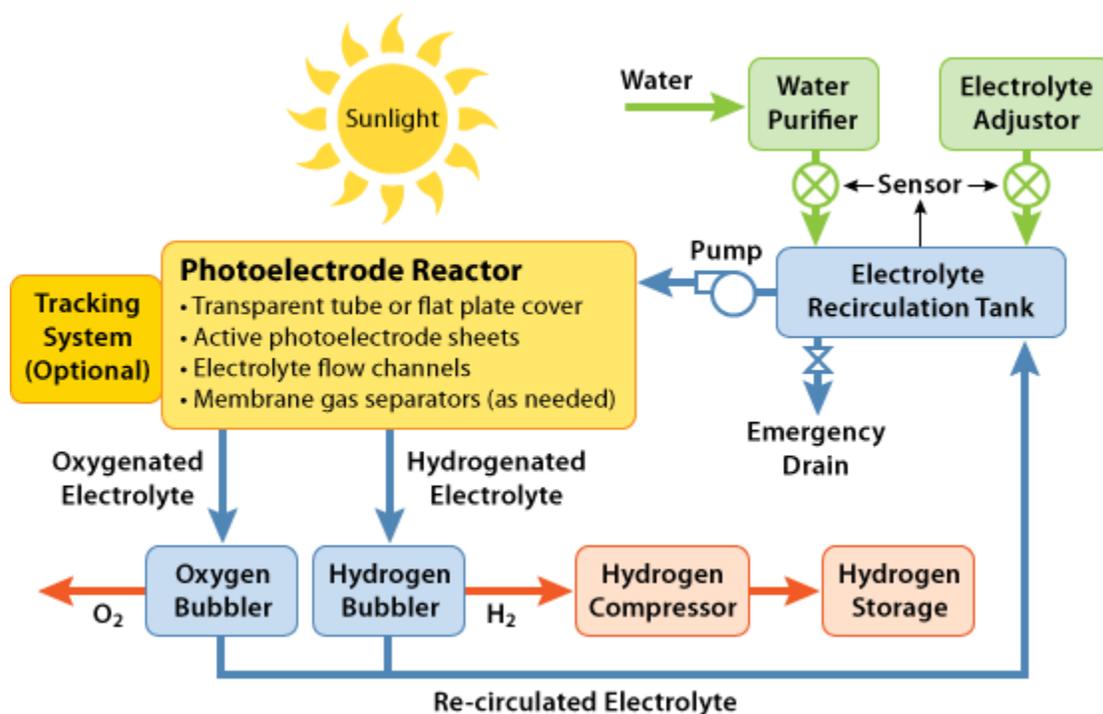


Figure 11-4: Photoelectrode System Block Diagram

Solar biological hydrogen production includes photobiological water splitting (direct water splitting) and photosynthetic bacterial production (solar-aided organic decomposition). Photobiological water splitting is a process to produce hydrogen from water using sunlight and specialized microorganisms, such as green algae and cyanobacteria (DOE, 2010b). Just as plants produce oxygen during photosynthesis, these microorganisms consume water and produce hydrogen as a byproduct of their natural metabolic processes. In photosynthetic hydrogen production, photosynthetic bacteria absorb solar energy to break organics down and release hydrogen. Solar biological hydrogen production technologies are in the early stages of development. The primary technical challenges for photobiological water splitting are identifying or developing microorganisms that can produce hydrogen at high rates with high solar energy conversion efficiency, and discovering oxygen-tolerant enzymes that can sustainably produce hydrogen (FreedomCar and Partnership, 2009b). Like photobiological water splitting, a major issue with photosynthetic bacterial hydrogen production is light utilization and hydrogen production efficiency. Another challenge is that most photosynthetic bacteria contain an enzyme that consumes produced hydrogen to support cell growth. This hydrogen reoxidation needs to be eliminated.

Solar thermochemical water splitting hydrogen production uses sunlight to produce temperatures up to 2,000°C to drive a series of chemical reactions that involve compounds reacting with water to produce hydrogen. The technologies of thermochemical hydrogen production are immature compared to traditional hydrogen production processes, such as natural gas reforming and coal gasification. The challenges of thermochemical hydrogen production include selecting the most

promising chemical reaction cycles, developing durable, inexpensive, and high-temperature resistance materials for the receiver, reactor, and thermal storage, and reducing the capital cost needed for facilities to concentrate solar energy (DOE, 2007a).

11.2.3 *Hydrogen Distribution and Utilization*

11.2.3.1 Hydrogen Fueling Infrastructure

Most U. S. hydrogen is produced at large industrial sites at or very near to where it is used (DOE, 2009g). Nearly all of it is for non-transportation use, with the major use being for petroleum refining. The most common ways to distribute the hydrogen are: (1) pipelines, (2) high-pressure tube trailers, and (3) liquefied hydrogen tankers (DOE, 2009g).

California is developing the beginning of a hydrogen fuel station network. The state had approximately 25 hydrogen stations as of 2008. The state has committed \$14.5 million in funding toward the development of 7 more stations throughout the state. Under AB 118, California is planning to invest an additional \$40 million towards hydrogen stations between 2009 and 2011. To meet the goal of 41,000 hydrogen vehicles on the road by 2017, it is estimated that 50 to 100 retail hydrogen stations will be needed, or roughly 10 new stations per year (CARB, 2009b; California Fuel Cell Partnership, 2009). Most of these stations produce hydrogen on-site by steam reforming of natural gas.

11.2.3.2 Hydrogen Fuel Cell and Internal Combustion Engine Vehicle Technologies

Hydrogen vehicles have been under development at a prototype level since the 1970s. A review of some of the early vehicle developments is provided in Norbeck et al. (1996). Hydrogen can be utilized in either an internal combustion engine or a fuel cell. Fuel cells are still primarily in the development stage and are still considerably more expensive than more traditional petroleum internal combustion engines.

Many of the major automobile manufacturers have conducted or are currently conducting research in the development of either hydrogen fuel cell or internal combustion engines. It is estimated, however, that there were only 200 hydrogen-powered cars in the United States as of October 2009, with most in California (Whoriskey, 2009). Honda has produced about 200 FCX Clarity passenger cars using compressed hydrogen and fuel cells for leasing in Southern California and Japan since the model showed up in 2007, but apparently has only leased a small number of these in the Los Angeles area. Honda stated that it could start mass producing vehicles based on the FCX concept by the year 2020. GM has leased 100 Equinox FCEV fuel cell/ battery hybrid vehicles installed with UTC Power fuel cells in California, New York, and Washington DC since 2007. Other companies involved in fuel cell development include Daimler and Hyundai.

For heavy-duty vehicle applications, SunLine, the transit provider in the Coachella Valley and Palm Springs, California area, has placed two fuel cell/ battery hybrid buses into regular service. Since 2000, when CARB approved regulations to reduce emissions from transit buses in California, several transit agencies within the state began developing programs to demonstrate zero-emission fuel cell buses. Funded by the DOE, AC Transit, the Santa Clara Transit

Authority, and the SunLine Transit Agency have participated in the fuel cell demonstration projects to evaluate the buses' performance, emissions, costs, and operating characteristics.

California continues to incentivize the development of hydrogen vehicles. The zero emission vehicle (ZEV) mandate requires each large auto maker to produce ZEVs by 2014. ZEVs include hydrogen fuel cell vehicles that have fast refuel and have ranges of 200 miles or greater, and battery electric vehicles with capabilities ranging from fast charge and 200+ miles range to neighborhood vehicles limited to 25 mph. The number of ZEVs marketed will depend on vehicle technology and functionality. In order to meet their environmental regulations, CARB has estimated that the percent of new vehicle sales for a combination of fuel cell vehicles and battery electric vehicles will need to increase from near zero levels in the 2020 timeframe to 100% of sales by 2040 (Cackette, 2010). Based on these projections, a combination of FCVs and BEVs are expected to represent approximately 87% of the in-use light-duty vehicle fleet by 2050. In January 2009, major auto companies shared their plans for deploying fuel cell passenger vehicles in northern and southern California. According to their combined projections, the number of passenger fuel cell vehicles deployed in Southern California will more than double each year between 2009 and 2017, when they expect the total to be over 41,000. In Northern California, they project 8,450 passenger vehicles by 2017.

Since hydrogen fuel cell technologies are not mature enough for widespread market use in vehicles, hydrogen internal combustion engine (HICE) may provide a mid-term approach for the transition from traditional internal combustion engine (ICE) vehicles to hydrogen fuel cell vehicles. A HICE vehicle uses hydrogen in a modified ICE instead of hydrogen fuel cells. One of the major drawbacks of HICEs has been the lower volumetric energy density of the hydrogen/air mixture, which results in reductions in power output. A review by CALSTART (2006), however, indicated that direct injection of hydrogen into the combustion chamber can partially compensate for this lower energy density, with some studies suggesting HICE's can have power densities that are similar to or are higher than those of their conventional counterparts. CALSTART (2006) also concluded that with adequate development of direct injection, HICE engines should be able to achieve efficiencies that meet or exceed those obtained for gasoline or diesel engines. Also, HICE engines should be able to achieve emission levels for partial-zero or near-zero classification with potentially less aftertreatment than would be required for more conventional vehicles.

Although HICEs development has been a lower priority for federal funding over the past decade, there has been some activity with HICEs in the areas of 1) using hydrogen or hydrogen blends as a fuel, 2) engine development. The early development of HICEs is reviewed in Norbeck et al. (1996). More recently, CALSTART reviewed the development of HICEs and relevant projects in this area for the US Department of Transportation (DOT) (CALSTART, 2006). A summary of some of the programs discussed in the CALSTART review and listed under the DOE (2010b) website is provided below. SunLine Transited Agency, in the Coachella Valley around Palm Springs, CA, has evaluated 20% hydrogen/CNG on their transit buses, under support from the FTA, US DOE, SCAQMD, and others. The tested vehicles were equipped with modified Cummins West B Gas Plus 5.9 L CNG engines. Westport Innovations conducted a demonstration project running hydrogen in a modified CWI 8.3L, C Gas Plus engine in the Vancouver area. The Idaho National Laboratory (INL) has been investigating the performance of

using hydrogen and hydrogen/CNG blends as a substitute fuel, under funding from the US DOE. DOE's Advanced Vehicle Testing Activity (AVTA) collaborated with Pinnacle West (holding company of Arizona Public Service) and Electric Transportation Applications (ETA) to evaluate the durability of a HICE design in both field and laboratory applications (DOE, 2010c). Several engine manufacturers have made an effort to develop ICE designs that are best suited for hydrogen applications. Ford has modified its 6.8L Triton™ V-10 gasoline engine for 100% hydrogen operation. In 2006, BMW launched the BMW hydrogen 7, the world's first sedan to run hydrogen and gasoline. Westport Innovations has been developing direct injection hydrogen injectors for their engines. MAN Nutzfahrzeuge AG delivered 14 HICE buses equipped with modified CNG engines to the Berlin transport authority.

Hydrogen has an extremely low energy density; hence storage on a vehicle is a critical issue. Hydrogen can be stored as a compressed gas, in a cryogenic tank as liquid hydrogen (LH₂), or in a metal hydride, but even the more compact storage systems such as LH₂ or metal hydride require 10 times the volumetric space for equivalent gasoline energy capacity (Norbeck et al., 1996). The cost of hydrogen on-board storage reflects the issues with storing a low energy fuel. Pearson et al. (2009) give a cost estimate of 250 Euros for the on-board storage of 50 liters of gasoline. For comparison, estimates of the costs of storage of hydrogen in a 700 bar tank with an equivalent energy capacity were between 2000 Euros (Eberle, 2006) and 10,000 Euros (Jackson, 2006). The US DOE (2010f) has been conducting hydrogen storage research since 2005 as part of the National Hydrogen Storage Project. They began a new effort in 2009 under the Hydrogen Storage Engineering Center of Excellence. These programs have focused on the applied research and development of low-pressure, materials-based technologies to allow for a driving range of more than 300 miles (500 km), while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. The hydrogen on-board storage cost targets for this program are \$133/kWhr for 2010 and \$67/kWhr for 2015.

Although hydrogen vehicles are expected to be more expensive than comparable gasoline vehicles for some times, some analysts have indicated that hydrogen fuel cell vehicles could be competitive with advanced technology vehicles of other types. A study by MIT researchers estimated that with minor improvements in system cost, a mass produced fuel cell vehicle with a 350-mile all-electric range is projected to cost only \$3,600 more than a conventional car and only \$700 more than an advanced hybrid (Kromer and Heywood, 2007). This was a lower incremental cost than a plug-in hybrid with a 30 mile all-electric range (\$4,300 more) or a full battery-electric vehicle (over \$10,000 more).

11.2.3.3 Fuel Cell Technology Development

Hydrogen fuel cells are the predominant technology being studied for future application in hydrogen vehicles. A hydrogen fuel cell is a galvanic cell (i.e., a battery) which converts the chemical energy of hydrogen into electrical energy by means of an electrical chemical process (Norbeck, 1996). A single fuel cell can only generate approximately 1 volt or less (DOE, 2008a). However, a series of individual cells can be stacked together to produce higher voltage for larger applications. Fuel cells using hydrogen as an energy carrier are one of the final technology steps for a hydrogen economy (DOE, 2003). Depending on the type of electrolyte used in the fuel cell, several fuel cell technologies are currently available, including polymer electrolyte membrane

(PEM), alkaline (AFC), phosphoric acid (PAFC), Molten Carbonate (MCFC), and solid Oxide (SOFC). Many of these technologies are utilized in other applications, including backup power, micro/portable power, remote power, and distributed power generation. Table 11-3 provides a comparison of the fuel cell technologies (DOE, 2010c). The PEM fuel cells have been the most heavily researched for transportation applications.

Table 11-3: Comparison of Fuel Cell Technology

Fuel Cell Type	Common Electrolyte	Operating Temperature	System Output	Electrical Efficiency	Combined Heat and Power (CHP) Efficiency	Applications	Advantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly-perfluorosulfonic acid	50 - 100°C 122 - 212°F	<1kW - 250kW	53-58% (transportation) 25-35% (stationary)	70-90% (low-grade waste heat)	<ul style="list-style-type: none"> ▪ Backup power ▪ Portable power ▪ Small distributed generation ▪ Transportation ▪ Specialty vehicles 	<ul style="list-style-type: none"> ▪ Solid electrolyte reduces corrosion & electrolyte management problems ▪ Low temperature ▪ Quick start-up
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100°C 194 - 212°F	10kW - 100kW	60%	>80% (low-grade waste heat)	<ul style="list-style-type: none"> ▪ Military ▪ Space 	<ul style="list-style-type: none"> ▪ Cathode reaction faster in alkaline electrolyte, leads to higher performance ▪ Can use a variety of catalysts
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 - 200°C 302 - 392°F	50kW - 1MW (250kW module typical)	>40%	>85%	<ul style="list-style-type: none"> ▪ Distributed generation 	<ul style="list-style-type: none"> ▪ Higher overall efficiency with CHP ▪ Increased tolerance to impurities in hydrogen
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 - 700°C 1112 - 1292°F	<1kW - 1MW (250kW module typical)	45-47%	>80%	<ul style="list-style-type: none"> ▪ Electric utility ▪ Large distributed generation 	<ul style="list-style-type: none"> ▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Suitable for CHP
Solid Oxide (SOFC)	Yttria stabilized zirconia	600 - 1000°C 1202 - 1832°F	<1kW - 3MW	35-43%	<90%	<ul style="list-style-type: none"> ▪ Auxiliary power ▪ Electric utility <ul style="list-style-type: none"> ▪ Large distributed generation 	<ul style="list-style-type: none"> ▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Solid electrolyte reduces electrolyte management problems ▪ Suitable for CHP ▪ Hybrid/GT cycle

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.

The application of hydrogen fuel cells provides many advantages. Hydrogen fuel cells use the chemical energy of hydrogen to produce electricity with water and heat as byproducts. As such, the biggest advantage of using a hydrogen fuel cell is its' essentially zero emissions, although some emissions are generated in the production of hydrogen. Another advantage of hydrogen fuel cells is that they are more energy efficient and may have the potential to transform up to 75% of energy in the hydrogen to energy used by the vehicle. Vehicles powered by hydrogen and fuel cells can be more than twice as efficient as internal combustion engines powered by gasoline or diesel (DOE, 2008a).

Current fuel cell technologies for transportation are all based on low-temperature PEM fuel cells. To meet the requirement of lowering PEM fuel cost and improving durability and efficiency, R&D has been focused on developing polymer electrolytes with increased conductivity, low-cost durable membrane materials, cathode catalysts, and cell hardware systems including bipolar plates and seals, and balance-of-plant components (e.g., compressor/expander, and thermal and water management). Major fuel cell research activities on membranes are identifying and developing ionomers/membranes with reduced raw material cost, identifying and developing ionomers/membranes with improved conductivity and mechanical/chemical/thermal stability over the entire temperature and humidity range, testing and characterizing membranes to

improve durability, and designing scalable membrane fabrication processes for producing membranes with mechanical/chemical/thermal stability over the entire temperature/humidity range (DOE, 2003). Research programs on electrodes include developing electrocatalysts with reduced precious metal loading, increased activity, improved durability/stability and increased tolerance to air, fuel and system-derived impurities, developing improved catalyst supports with reduced corrosion and material cost, and optimizing electrode design and assembly (DOE, 2007c).

One of the most critical disadvantages of hydrogen fuel cells is their cost. The DOE projected transportation fuel cell system costs over time are illustrated in Figure 11-5 (DOE, 2010c). Since the DOE promoted hydrogen fuel cell R&D research in 2004, significant accomplishments have been achieved in this area. For example, the estimated costs of automotive fuel cells have been reduced from \$275/kW in 2002 to \$61/kW in 2009 for a high production volume. The costs for automotive internal-combustion engine power plants are about \$25–\$35/kW, however (DOE website, 2010c). The DOE set an objective of developing a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation (DOE, 2007a). For vehicle applications, the life span of fuel cells needs to be roughly 5,000 hours to be comparable to traditional engines, and fuel cell systems need to be capable of functioning over the full range of vehicle operating conditions (40°C to 80°C) (DOE, 2003). The durability of fuel cell systems in the vehicles has been improved from 950 hours in 2006 to 2500 hours in 2010. The durability of fuel cell membrane electrodes (with cycling at <80°C) is now more than 7,300 hours, exceeding DOE's 2015 target of 5,000 hours (DOE website, 2010c). Other disadvantages of fuel cells for transportation include the size and weight of the cell system.

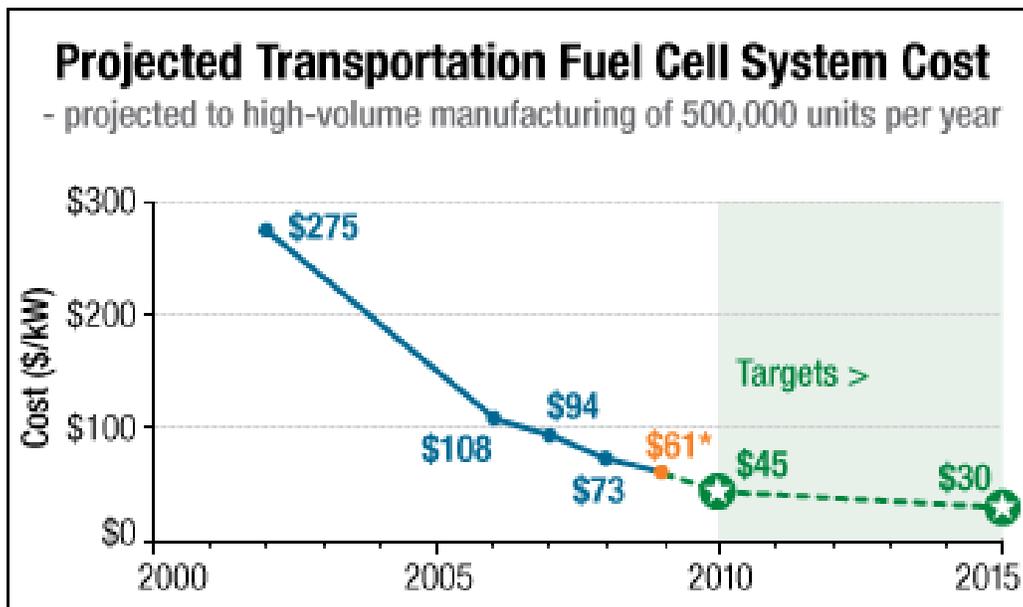


Figure 11-5. Projected Transportation Fuel Cell Cost

Although fuel cell technologies are not mature enough for full commercialization, some commercial and near commercial technologies and products for early market applications have

been developed in the past ten years. For example, 3M Company, under contract with the U.S. Department of Energy's Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program, has developed and commercialized a new membrane electrode assembly (MEA) that demonstrates superior performance and increased durability for fuel cell applications (DOE, 2009g). Funded by the U.S. Department of Energy's Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program, UTC Power developed The PureMotion® 120 Fuel Cell Powerplant (FCPP) and six new hydrogen fuel cell systems have been sold to power next-generation zero-emission transit buses (DOE, 2009g). Current commercial fuel cell technologies are listed in Table 11-4 (DOE, 2009g). While many novel technologies have been developed for various fuel cell configurations, most of the effort for transportation applications has been focused on PEM fuel cells. The major manufacturers of fuel cells for transportation are Ballard, Nuvera Fuel Cells, and UTC Power. Current U.S. commercially available fuel cells and fuel cell related products for transportation and their manufacturers are listed Table 11-5 (USFCC, 2009).

Table 11-4: Commercialized Fuel Cell Technologies

Technology	Company	Available Year
Advanced MEAs for Enhanced Operating Conditions	3M Co.	2007
Breakthrough Lifetime Improvements for PEM Fuel Cells	DuPont Fuel Cells	2005
Conductive Compound for Molding Fuel Cell Bipolar Plates	Bulk Molding Compounds, Inc.	2000
Corrosion Test Cell for PEM Bipolar Plate Materials	Fuel Cell Technologies, Inc.	2008
GCtool: Fuel Cell Systems Analysis Software Model	ANL	1999
GenCore® Backup Fuel Cell Systems	Plug Power Inc.	2008
Improved Fuel Cell Cathode Catalysts Using Combinatorial Methods	NuVant Systems Inc.	2006-2007
Integrated Manufacturing for Advanced Membrane Electrode Assemblies	BASF Fuel Cell, Inc.	
Novel Manufacturing Process for PEM Fuel Cell Stacks	Protonex Technology Corp	2008
PureMotion® 120 Fuel Cell Powerplant	UTC Power	2005
Scale-Up of Carbon-Carbon Composite Bipolar Plates	Porvair Advanced Materials, Inc	2003
XX25™: Portable Reformed Methanol Fuel Cell	UltraCell Corp.	2007
Improved Catalyst Coated Membrane (CCM) Manufacturing	Cabot Corp.	

Table 11-5: Commercial Fuel Cell Products

Manufacturer	Product Name	Application	Configuration
Ballard	Fcvelocity™-902	Transportation	PEM
Ballard	Fcvelocity™HD6	Transportation / Bus	PEM
Nuvera Fuel Cells	PowerFlow PFV-5	Industrial Vehicles	PEM
Nuvera Fuel Cells	Andromeda Fuel Cell Stack	Transportation	PEM
UTC Power	PureMotion® 120 Power System	Transportation	PEM

Hydrogen can also be produced on-board from feedstocks such as methanol, ethanol, or other hydrocarbon fuels. When a hydrocarbon/steam/oxygen mixture, or a carbohydrate/steam/oxygen mixture is passed over an appropriate catalyst the reactions can be exothermic, i.e., the reactions release heat. Thus, once the reactions are initiated the released heat serves as the source to sustain the reactions. This process is called autothermal reforming because the reactions proceed without the use of an external heat source and the hydrocarbons or carbohydrates, such as sugar, are converted (reformed) to CO, CO₂, H₂, and other compounds. This process can be carried out in microreactors and the hydrogen fed directly into a fuel cell (Norman, 2007).

Xuan et al. (2009) published a review of this technology. Most of the work has been carried out with methanol, ethanol, or methane as the feedstock, but there has been some work with higher molecular weight compounds including biodiesel. The lower molecular weight compounds are expensive but are the most efficient in hydrogen production. The higher molecular weights are less expensive but typically the unexpected side reactions deactivate the catalyst.

The catalyst is one of the most important components of the fuel processor. The catalyst nature, its support, precursor, and preparation method all affect the catalytic performance. Catalyst performance is also influenced by temperature, pressure, and gas composition.

Considerable research work is required to bring this technology into commercial production. The research includes:

- Improving the catalyst formulations to be more active toward production of hydrogen and less susceptible to deactivation.
- Defining the effect of supports, precursors, and catalyst preparation methods on catalyst performance.
- Determining the optimum temperature, pressure, and gas composition for hydrogen production.

While fuel cell development continues, it appears that the vehicle manufacturer development efforts are predominantly focusing on fuel cell technologies that will use hydrogen directly, rather than for on-board production of hydrogen.

Direct-methanol fuel cells (DMFCs) are a subcategory of proton-exchange fuel cells, which use methanol as a fuel instead of hydrogen. Although this technology is not a hydrogen technology per se, it is included here to provide a continuity with the discussion on the other hydrogen-based fuel cell technologies. DMFCs are classified as a zero-emission power system. In a DMFC, liquid methanol mixed with water is fed directly to the fuel cell anode, where it is oxidized and CO₂ and hydrogen ions are produced. At the anode, the electrons are generated as the electric output of the fuel cell. The positive hydrogen ions transport across the proton exchange membrane (PEM) and react with oxygen from the air to form water at the cathode. The reactions that take place in a DMFC are:



DMFCs were initially developed in the early 1990's, however, DMFCs were considered less attractive than PEM fuel cells for transportation due to their low efficiency and power density. The applications of DMFCs are limited by their low power. In the past two decades, the main progress in DMFC technology has been in the area of consumer goods applications, such as mobile phones, digital cameras or laptops, and portable power equipments, where energy efficiency are not critical (AMI, 2004). Some efforts have been made to develop DMFCs for off-road vehicles. In 2009, Nissan North America commercially deployed its Oorja Protonics Model III direct methanol fuel cell to power 60 electric-recharging forklifts at its Smyrna Tennessee manufacturing plant. This change provided significant savings in manpower in switching batteries and battery maintenance. The OorjaPac™ DMFC is equipped with a 3 gallon methanol fuel tank, and is capable of providing 20Kwh/day. Oorja Protonics recently launched its OorjaPac Model I DMFC with a 4.5 kW power output. The targeting market of OorjaPac DMFCs is the material handling industry.

11.3 Technical Limitations of Hydrogen as a Transportation Fuel

11.3.1 Technical Limitations for Hydrogen Feedstocks

While there are adequate supplies of natural gas for many years of hydrogen production, this does not contribute toward the goal of replacing fossil-based fuels with biomass-based fuels. If biomass is chosen as the feedstock for hydrogen production, then the limitation is likely to be the availability of the biomass in sufficient quantities at a reasonable cost. The most likely method for hydrogen production from biomass is through gasification, which is a costly production method that would require relatively large volumes of biomass within a reasonable distance of the gasifier for economic operation. It is also likely that there would be competing uses of the biomass for other alternative fuel pathways.

If any of the production methods for hydrogen from water, discussed in chapter 11.2.2, become economical, then feedstocks would be less of an issue, as there should be no shortage of water.

11.3.2 *Technical Limitations for Hydrogen Production*

All of the alternative hydrogen production methods are more costly than the steam reforming of natural gas. The National Research Council (NRC) reviewed the opportunities, costs, barriers, and R&D needs for a hydrogen economy (National Research Council, 2004). Michael Ramage, the chair of the review committee, summarized the conclusions of this study to the Science Committee of the US House of Representatives (The National Academies, 2004). The review committee concluded that for production “the required cost reductions can be achieved only by targeted fundamental and exploratory research on hydrogen production by photobiological, photochemical, and thin-film solar processes.” Some of the specific issues with various technologies for producing hydrogen from solar energy, such as solar PV-based electrolysis, solar photoelectrochemical water splitting, solar biological processes, and solar thermochemical water splitting, are discussed in chapter 11.2.2.

11.3.3 *Technical Limitations for Hydrogen Distribution and Utilization*

Unlike the traditional petroleum delivery system, the development of a system for delivering hydrogen from a central production facility to a refueling station to vehicles will be a significant challenge. In a fully developed hydrogen economy, delivery, storage, and dispensing of hydrogen at a high pressure will probably cost as much as production and will consume more energy. Distribution costs will be even more of a concern during the early transition years, when there is a lack of demand for hydrogen.

Cost estimates for developing an infrastructure for hydrogen vehicles vary depending on the study. In a recent study by the National Research Council (NRC, 2008), it was estimated that the total cost of deploying a national hydrogen network could be as high as \$200 billion, including \$55 billion in government aid through 2023. This network would be enough, however, to put only two million hydrogen cars on the road, in comparison with the total U.S. vehicle population of about 300 million cars and trucks. In an earlier 2002 study, an Argonne National Laboratory report estimated that the development of a hydrogen delivery infrastructure that could serve 40% of the light-duty fleet would likely cost over \$500 billion (Mintz et al., 2002). General Motors suggested that the costs can be reduced by concentrating on select urban centers (Mouawad, 2008). The company suggested that if 12,000 hydrogen stations were built in the largest 100 cities, that would put a station within two miles of 70 percent of the American population. That number of stations would be enough to fuel one million cars. An initial network of 40 hydrogen stations in Los Angeles, for example, would cost \$80 million based on a cost of \$2 million per station and cover the needs of that city in the early years of hydrogen deployment.

11.4 Environmental and Other Considerations

CARB (2009a) has evaluated the Well to Wheel (WTW) GHG emissions for various scenarios for hydrogen using the CA-GREET model. These results are provided in

Table 11-6. The results show that for nearly all examined scenarios, hydrogen provided lower carbon intensity values than either gasoline or diesel. The magnitude to the carbon intensity

reductions depends on a number of factors including whether the feedstock is renewable or not and where it comes from, how the fuel is produced, how the fuel is transported, and other factors in the utilization of the fuel, such as compression. For the production of hydrogen from renewable fuels, the carbon intensity values appear to be in a similar range to those of cellulosic ethanol, as discussed in chapter 5.4.

It should also be noted that while hydrogen vehicles may provide some reductions in tailpipe emissions relative to gasoline or diesel vehicles, these reductions would likely have a minimal air quality impact since advances in gasoline and diesel technology have already brought tailpipe emissions of the newest vehicles to very low levels.

Table 11-6: Adjusted Carbon Intensity Values for hydrogen.

Fuel	Pathway Description	Carbon Intensity Values (gCO ₂ e/MJ)		
		Direct Emissions	Land Use or Other Indirect Effect	Total
Gasoline	CARBOB – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	95.86	0	95.86
Diesel	ULSD – based on the average crude oil delivered to California refineries and average California refinery Efficiencies	94.71	0	94.71
Hydrogen	Compressed H ₂ from central reforming of NG (includes liquefaction and re-gasification steps)	142.20	0	74.82
	Liquid H ₂ from central reforming of NG	133.00	0	70.00
	Compressed H ₂ from central reforming of NG (no liquefaction and re-gasification steps)	98.80	0	52.00
	Compressed H ₂ from on-site reforming of NG	98.30	0	51.74
	Compressed H ₂ from on-site reforming with renewable Feedstocks	76.10	0	40.05

One of the primary espoused benefits of gaseous fuels such as CNG, LNG, and hydrogen are that they provide reductions in vehicle emissions. While this is true in an ideal sense, there have been significant advances in the emissions control technologies for both gasoline and diesel vehicles. Emissions from advanced gasoline vehicles meeting today’s most stringent regulations are significantly lower than those of past vehicles, and in some cases near the detection limits of existing emissions measurement methods. As of 2010, diesel vehicles are also being equipped with diesel particulate filters and either NO_x aftertreatment or changes in engine control strategies that control emissions to very low levels. Additionally, in some cases, it has been found that alternative fuel vehicles can have higher emissions than a corresponding gasoline or diesel vehicle if they are malfunctioning. Such high emissions from alternative fueled vehicles have been observed in a number of studies over the past two decades. Overall, given the advances in gasoline and diesel vehicle technology, it is likely that any emissions benefits from CNG, LPG, LNG, or hydrogen would be minimal past the near term.

11.5 Ongoing Research

Scientists at the University of Sheffield (2008) have been studying the production of hydrogen from a type of bacteria called Nostic. Nostoc fixes nitrogen and, in doing so, releases hydrogen that can then potentially be used as fuel. Using mathematical computer models, the Sheffield team have mapped the metabolism of this process. Understanding the metabolic mechanisms is an important step in understanding how the bacteria produce the energy needed in fixing the nitrogen, which is an energy intensive process.

Some photosynthetic microorganisms can produce hydrogen when illuminated. Prince and Kheshgi, (2005) reviewed the photobiological production of hydrogen. If this process can be made commercially viable the hydrogen would come from water and it might be more energetically efficient than growing, harvesting, and processing crops.

Iwuchukwu, et al. (2009) have generated a stable supply of hydrogen using a platinum catalyst and a protein complex for photosynthesis isolated from the thermophilic cyanobacterium *T. elongates* and a recombinant form of cytochrome-*c6* (cyt-*c6*) protein. Their system produced hydrogen for three months without special treatment or chemical preservatives. They estimate that the gross fuel production rate per unit area for these complexes “exceeds the best biomass-to-fuel schemes by a factor of 25.”

The feedstock for photochemical and thin-film solar process hydrogen production is water. The photochemical process involves the photodecomposition of water to hydrogen and oxygen in the presence of a catalyst and a light source. There are two recent articles discussing the photochemical process Arachchige et al. (2008) and Kanan and Nocera (2008).

All of the above work has been carried out in laboratory apparatus. Therefore there is considerably more research required in all of the above areas before any of them can be considered for advancement to a pilot stage.

11.5.1 *DOE Program*

In 2004, with U. S. DOE cost-sharing funding assistance, four automobile manufacturer-energy company partnerships started a 5 year program to validate hydrogen fuel cell vehicle and fueling technology (NREL, 2007). The DOE establish goals for various parameters for various future years. Some of the goals are tabulated in Table 11-7. The on-site generation of hydrogen was either by steam reforming of natural gas or via electrolysis of water (Wipke et al., 2009). In general, the impurities in the produced hydrogen from electrolysis of water were greater than those produced by the steam reforming of natural gas. As part of this effort, NREL set up a data-collection and analysis system that collected extensive data on the demonstration fleets and infrastructure. Every six months this composite data was posted on the website [www.nrel.gov/hydrogen/cdp_topic.html] (Wipke, et al., 2009). The program was completed in September 2009. The results for the actual estimates relative to the program goals are provided in Table 11-7.

Table 11-7: Some goals and results for DOE/Industry 5 year hydrogen demonstration test

Parameter	Year / Goal		Actual Estimate	
			Gen 1 Vehicles	Gen 2 Vehicles
<10% voltage degradation	2006 / 1000 hrs	2009 / 2000 hrs	<820 hrs	<1020 hrs
Vehicle Range	2009 / 250 mi	2015 / 300 mi	100 – 190 mi	200 – 250 mi
Power density	2010 / 220 w/l	2015 / 220 w/l	150 – 215 w/l	130 – 215 w/l
Specific Power	2010 / 325 w/kg	2015 / 325 w/kg	130 – 220 w/kg	180 – 260 w/kg
Cold start up time from -20° C soak	2010 / 30 sec to 50% rated power	2015 / 30 sec to 50% rated power	For 12 hr soak at -9 to -20°C ~10 - ~280 sec to drive away ~90 - ~520 sec to equilibrium	
Fuel cell system efficiency	60% at 25% power		51 – 58%	53 – 59%
	50% at 100% power		30 – 54%	42 – 53%
Wt% hydrogen storage	2007 / 4.5%		@350 bar / 2.9 – 3.8%	
	2010 / 6%		@700 bar / 2.5 – 4.4%	
	2015 / 9%			
Volumetric capacity of hydrogen storage	2007 / 0.037 kg/l		@350 bar / 0.017 – 0.018 kg/l	
	2010 / 0.045 kg/l		@700 bar / 0.018 – 0.024 kg/l	
	2015 / 0.081 kg/l			
Hydrogen tank cycle life	2007 / 750 cycles		2000 – 11000+	5000 - 15000
	2010 / 1000 cycles			
	2015 / 1500 cycles			
On-site H ₂ production eff from natural gas	2010 / 72% of LHV 2015 / 74% of LHV		Average station efficiency = 52% of LHV	
On-site H ₂ production eff from electrolysis	2012 / 69% of LHV 2017 / 73% of LHV		Average station efficiency = 44% of LHV	
Fueling rates	2006 / 1 kg/min	2012 / 1.66 kg/min	@350 bar / ave = 0.82 kg/min with 29% >1 kg/min @700 bar / ave = 0.62 kg/min with 3% > 1 kg/min	
H ₂ quality index	99.97%		For years 1 through 4 >99.98%+ from natural gas From Electrolysis 99.92 – 99.96% for year 1 99.73 – 99.99% for year 2 99.99%+ for year 3 99.97 – 100% for year 4	
Fuel cell power density	2010 and 2015 / 650 w/l		320 – 395 w/l	285 – 395 w/l
Fuel cell specific power	2010 and 2015 / 650 w/kg		190 – 315 w/kg	305 – 405 w/kg
H ₂ compression efficiency	2010 and 2015 / 94%		Average station compression efficiency = 89%	
Power drop	None		68% of in operation stacks have >10% power drop	95% of in operation stacks have >10% power drop
Hours to reach OEM low power operation limit	None		27% > 2000 hrs	9% > 2000 hrs
Hours to fuel cell stacks 30% voltage drop	None		~1700 hrs	~1400 hrs

Note: Gen 1 vehicles are pre 2008 models and Gen 2 vehicles are 2008 and newer vehicles. Various design changes were made between the two generations of vehicles to improve the overall performance of the vehicles, including

the maximum time to 10% voltage generation, the average fuel cell durability, the maximum hours of operation, the driving range, the fuel economy, the fuel cell efficiency, etc.

11.6 Research Roadmap Recommendations for Hydrogen

Of the gaseous fuels, hydrogen typically receives the greatest interest as a long term transportation fuel source. To make hydrogen fuel a viable transportation fuel option, considerable improvements will be needed in the production technology, vehicle technology and distribution infrastructure. Since the majority of the DOE goals in Table 11-7 were not met, additional research towards achieving these goals is required. Some research funds will need to be directed towards production of hydrogen from a renewable resource. The cost of producing vehicles capable of running on hydrogen still needs to be substantially lowered, and could include fuel cells as well as internal combustion engine configurations. There will also continue to be a need for an infrastructure for the safe transportation and distribution of hydrogen, although this is outside the scope of activities that would be funded through PIER funds.

Although there are still critical barriers to the continued development of hydrogen as a transportation fuel, it appears that hydrogen could play an important role as a transportation fuel in the longer term 2040 to 2050 timeframe. California is already investing in a hydrogen fuel infrastructure, and there is also some industry investment in vehicle technology. Nevertheless, it appears unlikely that hydrogen will have a significant impact as a transportation fuel over the next 10-15 years. Overall, it is recommended that hydrogen be included in the portfolio of fuel technologies to be supported by PIER. Hydrogen should be considered a longer term transportation solution, targeting a time horizon in the 2030-2050 period. PIER should continue to monitor developments in hydrogen production techniques and vehicle technology. Key areas for PIER funding should include fuel cell technology and hydrogen production techniques, such as solar energy. The development of hydrogen fuel production technologies would be the most appropriate area for funding within the fuels section of the PIER-Transportation Research Area, while the funding of fuel cell related projects would be more appropriate for funding under the vehicle technology section of the PIER-Transportation Research Area.

12 Other Advanced Technologies

12.1 Introduction

This chapter reviews some advanced technologies that are still in the preliminary research and development stage. While these technologies would not likely be viable in the near- or mid-term, it is nevertheless useful to review their development and status in terms of what future fuels might meet our long-term fuel needs.

12.2 Carbon Dioxide Conversion to Hydrocarbons

CO₂ can be converted into hydrocarbons via a process known as electrocatalytic gas-phase conversion. In this process, CO₂ is confined inside carbon micropores that contain an active catalyst of noble metal nanoclusters. The reaction is catalyzed when an electric current flows through the catalyst. The resulting reaction process can reduce gaseous CO₂ to a series of hydrocarbons that are remarkably similar to those of a Fischer-Tropsch (FT) process and/or alcohols, such as methanol.

On the commercial side, HS Orka has started to build a plant to produce methanol for transportation fuel using the CO₂ released from their geothermal power plant at Svartsengi in Iceland. It was estimated that the methanol production will begin near the end of 2010 and the facility will be capable of producing around 4.2 million liters of methanol per year at its full capacity. In late 2008, Mitsui Chemical Inc. of Japan, in collaboration with the Research Institute of Innovative Technology for the Earth in Kyoto, began to construct a pilot plant for deriving methanol from industrial CO₂ emissions at the company's Osaka facilities. The hydrogen used in this process is produced by an anatase titania photocatalyst. The process is illustrated in Figure 12-1. The company expects an annual yield of approximately 33,000 gallons of methanol. Blue Fuel Energy of British Columbia is planning to build a 1.5 million liters/day methanol production plant in the Pine River valley. Using an off-the-shelf, world-class scale methanol plant, this facility will utilize hydro and wind generated electricity, water from the river, and about 2100 tons of CO₂, emitted from the Spectra Energy's natural gas processing plant in the valley, to produce Blue Fuel methanol for biodiesel feedstock and gasoline blend (Blue Fuel Energy Website, 2010).

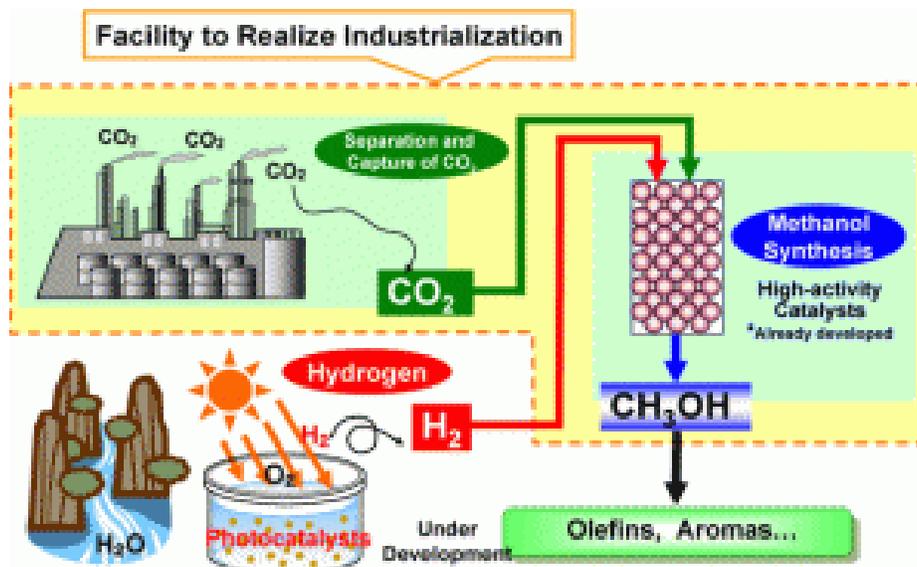


Figure 12-1. Process Mitsui CO₂ to Methanol

Other work in this area is being conducted at a research level. Some research efforts in this area have focused on developing catalysts for CO₂-to-methanol conversion. Scientists at Institute of Bioengineering and Nanotechnology (IBN) of Singapore have successfully transformed CO₂ to methanol using a newly developed organocatalyst, N-heterocyclic carbene (NHC) (Riduan et al., 2009). This stable, non-toxic and low-cost organocatalyst can activate CO₂ under relatively mild conditions in dry air, and then convert CO₂ to methanol.

The EU provided €875,246 (US\$1.1 million) in funding for a three-year project to study the gas-phase electrocatalysis of CO₂ to Fischer-Tropsch (FT)-like products (C₁-C₁₀ hydrocarbons and alcohols). This work began in 2004 and included researchers from the University of Messina, Italy, Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany, Université Louis Pasteur in Strasbourg, France, and University of Patras in Patras, Greece. These researchers found that it was possible to produce higher carbon hydrocarbons (C₈ to C₉) using this method, with the productivity depending upon a number of factors, such as catalyst, electrolyte and flow rates (Centi, 2006).

In earlier research, Liu et al. (2001) used a dielectric-barrier discharge (DBD) plasma to convert methane/CO₂ mixtures to a syngas containing ethylene, acetylene, and propylene, liquid hydrocarbons, plasma-polymerized film, and oxygenates. The product selectivity depended upon the plasma reactive conditions, the CH₄/CO₂ ratio, and the catalyst applied. Increasing the DBD power level from 200 W to 700 W increased the conversion of CH₄ from ~34% to ~74% and the conversion of CO₂ from ~30% to ~62%. The higher power levels also increased the yield of higher molecular weight hydrocarbons and decreased the yield of the lower molecular weight hydrocarbons. In other research, Nam et al. (1999) passed H₂ and CO₂ (3/1 mixture) through a stainless steel fixed bed flow reactor filled with catalyst. The products included CO, CO₂, water, and hydrocarbons, with methane being the dominant hydrocarbon.

In more recent research, Varghese et al. (2009) have produced methane and some higher hydrocarbons by exposing titania nanotubes surfaces loaded with cocatalysts to natural sunlight. The reaction was carried out inside a stainless steel chamber equipped with a quartz window with 99.99% pure CO₂. They do not provide any estimate of the cost of the feedstock (99.99% pure CO₂) nor of the processing costs. Dr. Grimes has received a \$300,000 award from the National Science Foundation (National Science Foundation, 2009) to further this work. The award is estimated to cover a period from September of 2009 through August of 2012. In other research, Hussain and Rahman (2009) used a trimetallic nano catalyst and a fixed bed catalytic process to convert CO₂, steam and 1% H₂ to ethanol and propyne. Over a period of 0.5 hours to 3.0 hours at 450°C, the percent ethanol production in the reactor increased from 15 to 36 and the percent propyne production increased from 20 to 41.

The Advanced Research Projects Agency-Energy (ARPA-E) announced in December of 2009 that they will fund research into novel ways to make renewable fuels under a new Electrofuels program (Bullis, 2009). Funding is being considered for (1) pairing microorganisms which use electricity to form organic molecules with solar cells, (2) using extremeophiles, microorganisms living in extreme environments, such as hot and acidic water, which draw energy from sources such as metal sulfides and use carbon dioxide to form proteins and lipids. With these technologies, it may be possible to modify the metabolic pathways so that the organisms produce fuels directly.

Research in this area is still in a very preliminary stage and it appears that other technologies are more viable for the longer term 2050 timeframe, so this area is not recommended for PIER funding as a long term fuels technology. This area should continue to be monitored to identify any potential breakthroughs that might make this technology a more viable option for the longer term timeframe, and hence worthy of reevaluation for funding.

12.3 “Fuels from Sunlight” Program

The US DOE (DOE, 2010d) has recently awarded funding of \$122 million over five years to establish an Energy Innovation Hub aimed at developing revolutionary methods to generate fuels directly from sunlight. The award was won by the Joint Center for Artificial Photosynthesis (JCAP), to be led by the California Institute of Technology (Cal Tech) in partnership with the U.S. Department of Energy's Lawrence Berkeley National Laboratory (Berkeley Lab). Other participating institutions include SLAC National Accelerator Laboratory, Stanford, California; the University of California, Berkeley; the University of California, Santa Barbara; the University of California, Irvine; and the University of California, San Diego. The Hub will be funded at up to \$22 million this fiscal year. The Hub will then be funded at an estimated \$25 million per year for the next four years, subject to Congressional appropriations.

The goal of the Hub is to develop an integrated solar energy-to-chemical fuel conversion system and move this system from the bench-top discovery phase to a scale where it can be commercialized. The 'artificial photosynthesis' process/system would essentially emulate the inner workings of plant life to produce a transportation fuel. JCAP research will be directed at the discovery of the functional components necessary to assemble a complete artificial

photosynthetic system: light absorbers, catalysts, molecular linkers, and separation membranes. The Hub will then integrate those components into an operational solar fuel system and develop scale-up strategies to move from the laboratory toward commercial viability. The ultimate objective is to drive the field of solar fuels from fundamental research, where it has resided for decades, into applied research and technology development, thereby setting the stage for the creation of a direct solar fuels industry.

While development is still needed in this area before it is commercially viable, it appears that there is good momentum at the Federal level to move this program forward. Research in this area would also tie in closely with the development of hydrogen fuels as a long term transportation solution, as discussed in chapter 12.6.2. As such, it is recommended that PIER direct some of the funding for its long term development efforts to this area.

12.4 Methane Hydrates

Methane hydrates are the most abundant natural form of a clathrate. Clathrates are substances where one material forms an open solid lattice that encloses another material, without chemical bonding. In this case, methane, the major component of natural gas, is physically trapped in a cage-like lattice of ice crystalline solids (DOE, 2010e). Methane hydrates form at low temperatures and high pressures and are thermodynamically stable within certain ranges of pressure and temperature (Desa, 2001). Methane hydrate can be converted to methane gas and water when it is warmed up or depressurized (DOE, 2007e). The energy density of methane hydrates is very high, a 1 cubic foot (0.028 m³) block of solid methane hydrate will release approximately 160 cubic feet (4.53 m³) of methane at surface temperature and pressure (NETL, 2007). It is estimated that the amount of carbon stored in methane hydrates is about 10,000 gigatons globally, which exceeds the combined amount of carbon in all known fossil fuels (Desa, 2001). With natural gas providing about 23% of the energy consumed in the US, methane hydrates can be a potential energy source to meet the increasing demand of energy.

Large resources of methane hydrates are available globally. Approximately 400 trillion cubic feet of potential natural gas from methane hydrates are stored on the earth (DOE, 2007e) According to the Department of Interior's US Geological Survey in 2008, an estimate of 85 trillion cubic feet or more of methane hydrates can be recovered from the Alaska North Slope (USGS, 2008). In the Gulf of Mexico, more than 6,000 trillion cubic feet of methane hydrates resources are available according to a recent NETL report (NETL, 2009). Generally, two types of methane hydrate deposits exist: under Arctic permafrost, where methane hydrates are generated by bacterial activity in the shallow sediments, and beneath the ocean floor, where water is more than 500 ft deep and methane hydrates are formed by geological processes. Figure 12-2 shows the global location of known or inferred methane hydrates (DOE, 2007e).

Harvesting methane hydrates and economically distributing them can be challenging. Since methane hydrates are solid, they cannot be transported in pipes without converting it to gas or liquid format. Dissociating methane from a hydrate structure plays a key role in the production of methane hydrates. Similar to oil production, thermal stimulation, depressurization, and inhibitor injection are some of the possible methods to recover methane.

In the thermal stimulation process, two wells are drilled and a hot fluid (water or steam) is pumped down through one well to dissociate the methane hydrate (Desa, 2001). The disassociated methane can be pumped up the other well. The tremendous amount of energy required to heat the water increases production costs. The hot fluid is unlikely to transfer heat throughout the methane hydrate-bearing layer and thus recovery efficiency could be very low. Also, because methane hydrate-bearing layers are typically 500 feet or more beneath the surface of the oceans, the temperature of the hot fluid will be reduced by the cold ocean water.

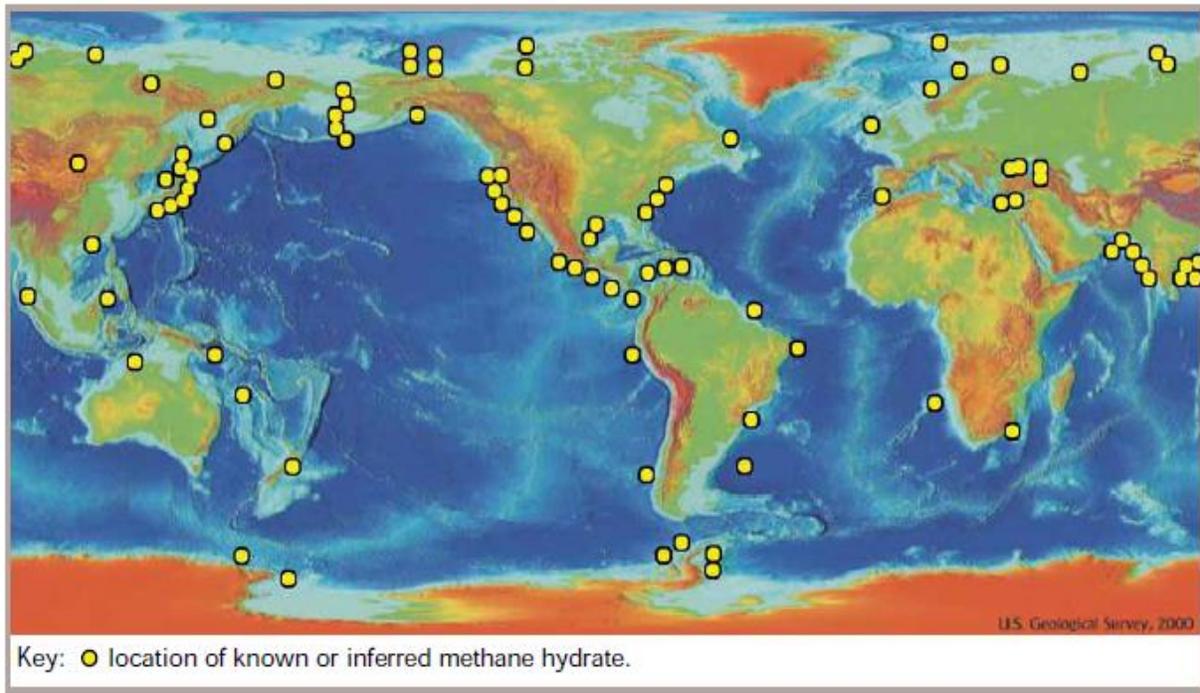


Figure 12-2: Geographical Distribution of Methane Hydrates

In the depressurized process, the pressure in the well is lowered which makes the methane hydrates unstable and they dissociate. The depressurized process is usually applied to geologically created methane hydrates deep under the sea. The shortcoming of this method is that the whole methane hydrate layer may not fully be depressurized and completely recovered (<http://www.mh21japan.gr.jp/english/mh/06seisan.html>).

In the inhibitor injection process, an inhibitor such as methanol is injected from the surface down to methane hydrate layers, which shifts the methane hydrate pressure-temperature equilibrium causing release of the methane (Desa, 2001). An issue with this process is that to ensure full recovery a method would have to be developed to inject the inhibitor evenly throughout the entire methane hydrate-bearing layer.

Currently, commercial large scale production of methane hydrates is not available. However, many research programs have been focused on detecting and quantifying methane hydrate

deposits, and the demonstration of production methods (DOE, 2009h). The methane hydrate R&D field projects include, conducting production testing on the North Slope of Alaska, deep-water drilling in the Gulf of Mexico, and forming a cooperative international study to measure methane hydrate deposits off coasts of India. ConocoPhillips will conduct the first field trial in the Prudhoe Bay region to produce methane hydrates by injecting CO₂ into the reservoir to replace methane molecules in the gas hydrate (DOE, 2008b).

Another challenge to methane hydrate production is to understand methane hydrate's potential impacts as a geohazard. Since methane is a greenhouse gas and has a very high Global Warming Potential (GWP) index, the release of methane can cause global climate change. The production of methane may also have impacts on the geological environments (Desa, 2001).

Methane hydrate research is still in the early stages of development and has the additional disadvantage that it is not a renewable resource (see chapter 2.9). As such, this is not an area recommended for funding with PIER monies. Continuing research in this area would be more appropriately funded at the Federal level and by those private companies looking to produce this resource.

13 Other Considerations

This chapter reviews some advanced technologies that are still in the preliminary research and development stage. While these technologies would not likely be viable in the near- or mid-term, it is nevertheless useful to review their status in terms of what future fuels might meet our long-term fuel needs.

13.1 Characteristics of the Vehicle Fleet

The makeup of the vehicle fleet is one of the most critical factors in evaluating what fuels/technologies will have the best chance of success in the future. It is expected that a range of technologies will be needed as the in-use vehicle fleet transforms to meet air quality and greenhouse gas reduction targets. This will include conventional gasoline and diesel vehicles, hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), battery electric vehicles (BEVs), and fuel cell vehicles (FCVs). Some estimates of the changes that will be needed in the vehicle fleet between now and 2050 to meet the State's current goals by CARB are shown in Figure 13-1 and Figure 13-2, which show the percentage of new vehicle sales by technology and year and the percentage distribution of the in-use vehicle fleet by technology and year, respectively. These estimates show that the predominant fraction of the in-use vehicle fleet from now through the 2020-2030 timeframe will be a combination of conventional vehicles and HEVs. More advanced technology vehicles, such as PHEVs, FCVs, and BEVs will represent a steadily increasing percentage of the new vehicle sales from 2020 to 2040, when they are estimated to represent 100% of new vehicle sales. These advanced technologies are expected to represent approximately 25% of the in-use fleet by 2030 going to 87% of the fleet by 2050.

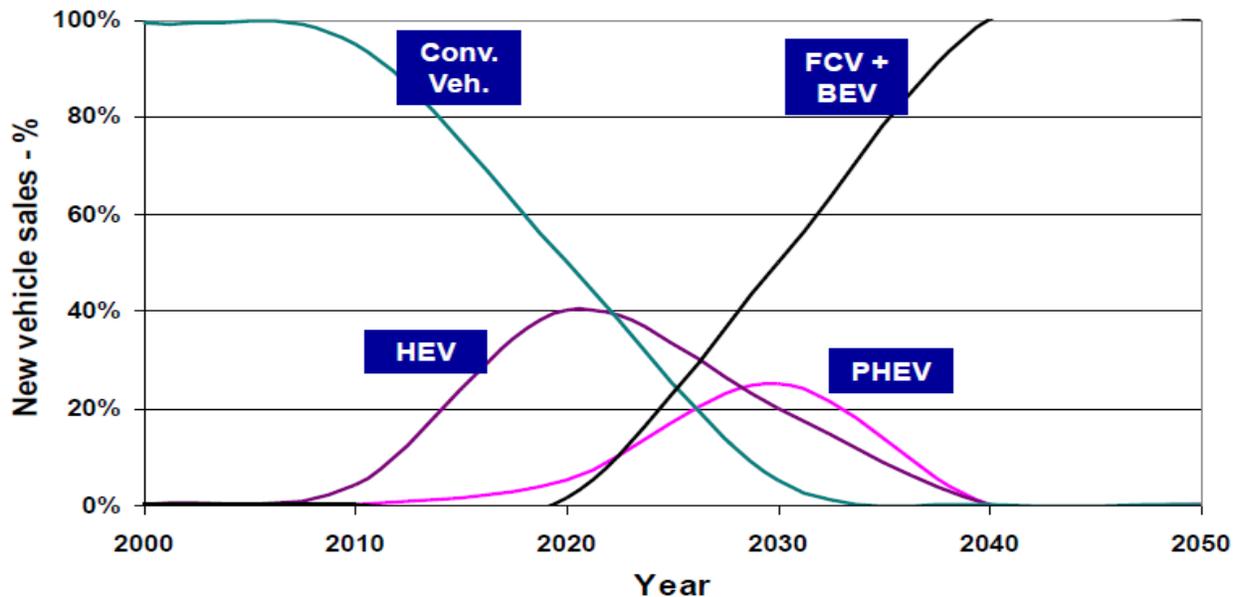


Figure 13-1. CARB Estimates of the Distributions of New Vehicle Sales from 2000-2050.

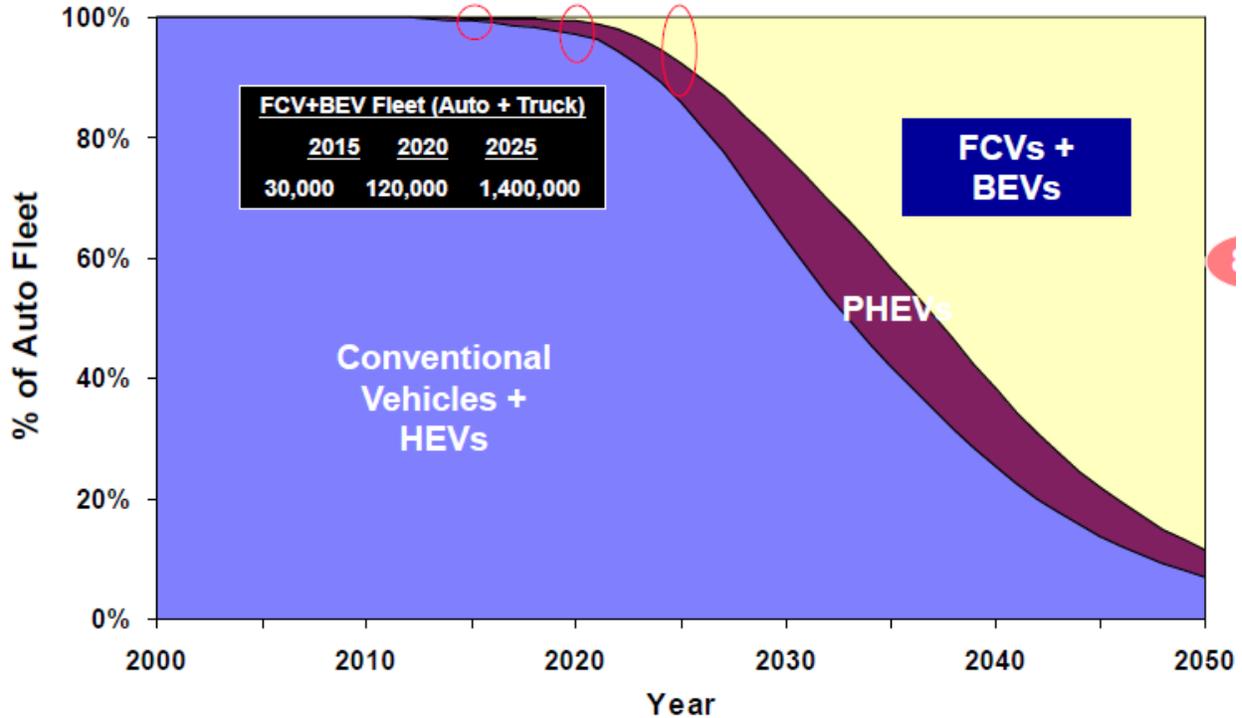


Figure 13-2. CARB Estimates of the Distributions of Different Vehicle Technologies in the In-use Fleet.

While these estimates represent a possible scenario for the penetration of HEVs, PHEVs, BEVs, and FCVs, it probably represents a more optimistic view on the potential growth of these technologies. Irregardless of how optimistic these estimates are on the development and implementation of advanced electric/battery/hydrogen technologies, it is evident that liquid fuels will remain the predominant fuels for at least the next 30 years. Thus, funding resources for this time period should be allocated towards technologies and fuels that will produce renewable liquid-based fuels with low carbon intensities and that can be produced within the State. The anticipated large percentages of conventional fueled vehicles would also dictate that these fuels would need to be compatible with conventional vehicles as well. This would include ethanol, other alcohols such as methanol and butanol, renewable diesel, such as biodiesel, Fischer-Tropsch diesel, or hydrogenated renewable diesel, or synthetic gasoline. Fuels such as CNG, LPG, hydrogen, DME would all require the introduction of specialized vehicles and fueling infrastructure that will not likely be feasible over the next 10-15 years with the exception of commercial fleets. Thus, our recommendation is that the development of these fuels not be ignored but, from a pragmatic point of view, have a lower priority for research funding in the near-term.

While this roadmap does not directly deal with vehicle technologies, it is worthwhile to note that the development and expansion of renewable liquid fuels would likely be associated with advances in vehicle technologies such as those employed in hybrid or electric vehicles. Drivetrains for electric/hybrid configurations can utilize a direct connection between the electric motor and the wheels. This configuration eliminates the need for a transmissions, which can

provide smoother acceleration and smoother braking, provide higher torque over a larger range of speeds during acceleration, allow for the recovery of some energy lost during braking through regenerative braking, and provide better energy efficiency. While a discussion of synergies between vehicle technologies and liquid fuels is outside the scope of this work, this may be a consideration in evaluating future research efforts in fuels development by PIER.

13.2 Feedstock Availability and Technology Scalability in Meeting Transportation Fuel Needs

One of the most important considerations in evaluating technologies/fuels is the ability to meet the actual needs in the transportation fuels market. It is important to recognize the State of California uses over 16 billion gallons of liquid transportation fuels a year. Thus, any viable mix of energy conservation, feedstock, fuel production, public transportation improvement must have the potential to meet this energy demand in the future. From the standpoint of fuel production technologies, it is also important that the technologies being supported can be scalable to meet these needs, or at least be a legitimate part of a portfolio of technologies that could meet these needs.

The availability of feedstock in California will be an important driving factor in evaluating the technologies/fuels that will have the highest probability of success. From the results of previous studies, the distribution of potential feedstocks within the State will likely be regionally dependent. Forestry residues will likely be the predominant source in northern California. Agriculture biomass will be more prominent in the central part of the State. In urban areas and in the southern California area, municipal solid waste will likely be the most readily available feedstock source. Other feedstock sources such as algae or drought-tolerant energy crops may have a broader distribution within various parts of the state. In addition to the broader regional questions with respect to feedstock, it is also important to understand concentration of feedstock that might be available within a reasonable transport distance to a production facility. While regional studies of potential feedstocks within California have been performed, there have been few/no studies of the optimal locations for facilities that would provide the greatest concentration of feedstock within a reasonable transportation distance. The local potential for various biomass feedstocks will be a critical factor in determining if production facilities can be cost effective at various locations. Given the critical nature of this question, a study to characterize the local potential of various biomass feedstocks should be one of the highest research priorities, since this information will be central to determining what production technologies would be viable or not.

13.3 Energy Density of the Transportation Fuel

The volumetric and gravimetric energy density of a fuel is an important consideration in terms of storage on-board a vehicle, vehicle range, and operational costs for the vehicle owner. The volumetric/gravimetric energy density is the amount of energy stored in a unit volume/mass of a given fuel. The higher the volumetric energy density for a fuel, the more energy it can release from the same amount of volume. The net system volumetric and gravimetric energy densities for various transportation fuel options are summarized in Figure 13-3 (Pearson et al., 2009). In this chart, the on-board system package volumes and weights are included in the net volumetric

and gravimetric energy densities. This Figure clearly shows that diesel and gasoline have the highest energy densities on both a volumetric or gravimetric basis. Alcohols and alcohol blends have the next highest energy densities, with the gaseous fuels having the lowest energy densities. In both the case of the alcohols and the gaseous fuels, the energy density deficits relative to gasoline and diesel fuels are significant, and this deficit would have to be offset to make these fuels acceptable to the consumer market. Lead-acid, nickel-metal hydride, and lithium ion batteries offer the lowest volumetric and gravimetric densities, as shown in Figure 13-3. It is also worth noting that while hydrogen may have the highest energy density on a per unit mass basis as a molecule, bulky and heavy containers are needed to store hydrogen at high pressures. This brings the on-board hydrogen volumetric and gravimetric energy densities down to much lower levels in the chart.

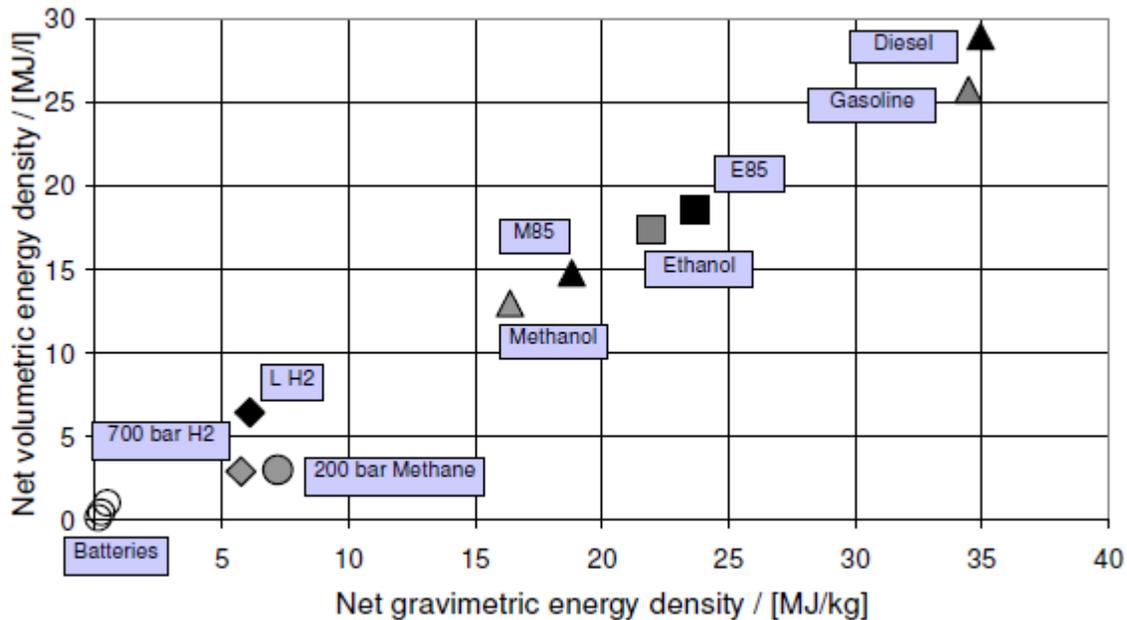


Figure 13-3. Net system volumetric and gravimetric energy densities for various on-board energy carriers (based on lower heating values).

13.4 Environmental Issues

Environmental issues, such as greenhouse gas reductions and improvements in air quality, are some of the most important driving factors for the development of alternative fuels. Since environmental factors are critical to the promotion of alternative fuels, it is important to evaluate the environmental benefits/liabilities of various alternative fuels as they continue to be developed.

One important methodology in evaluating environmental impacts of various fuels is well-to-wheel and biomass production-to-wheel models. Such models continue to be developed and refined as more information on the factors relating to the production/use of various alternative

fuels becomes available. The results of the models are very dependent upon the inputs to the model, however, and very often those using the models have to make multiple assumptions about the value of the various inputs. Therefore it is imperative that such model evaluations be very carefully reviewed by an independent body. The model results should be carefully scrutinized to ensure that all the input values are tabulated in the report and that they are all reasonable values. If possible, the model outputs should be verified by experimental measurements. It is also worth noting that while CARB has done well-to-wheel evaluations of the carbon intensity values for some fuels/processes, other fuels, such as those derived from thermochemical processes have yet to be evaluated by the state. Additional PIER research funds could help address environmental impact analyses for various fuels and facilitate the advancement of fuels where such analyses have not been conducted by the State. Such analyses could be beneficial in determining how PIER funds should be distributed between thermochemical and biochemical processes.

Every method of converting biomass to fuel produces non fuel compounds that may have an adverse effect on air, water, or land. Depending on their ultimate disposal method, these non fuel compounds need to be assessed so they can be used or disposed of without an adverse effect on the environment. Minor components can also potentially have adverse effects on vehicle performance or produce toxic emissions when the fuel is burned. In California, these issues are addressed through the multimedia evaluation process. This process includes a comprehensive evaluation of any potential significant adverse impacts on public health or the environment, including air, water, or soil, that may result from the production, use, or disposal of a new fuel. This process is very extensive and costly. While worth mentioning, the funding of such multimedia evaluations is beyond the scope of PIER's efforts, since fuels undergoing multimedia evaluation are typically relatively near the point of commercialization.

13.5 Development of Comprehensive Biorefinery Facilities

In developing a long term future for fuel production, it is important to develop facilities that will process the feedstock in a comprehensive way. In this way, such fuel production facilities would be comprehensive biorefineries. This would include the processing of residual components to produce heat or energy that will meet a portion of the overall system requirements. The viability of such facilities could be evaluated with comprehensive process economic models.

14 Summary and Conclusions

Increasing the use of alternative fuels is an important priority within the State and is the subject of a number of legislative initiatives. The PIER Transportation Research Area (PIER-TRA) of the California Energy Commission (CEC) contracted with CE-CERT to develop a roadmap to guide its research efforts into the near and medium term. As part of the roadmap development process, CE-CERT produced several Alternative Fuels Technology Snapshot white papers addressing the state of various alternative fuel technologies in the areas of resource cost and supply potential, fuel production, distribution and utilization roadblocks, gap analysis and technology assessment, and recommendations of fuel pathways. These white papers formed the building blocks for this roadmap. A summary of the findings of this work is as follows:

General Factors or Considerations

Vehicle Technology

The makeup of the vehicle fleet is one of the most critical factors in evaluating what fuels/technologies will have the best chance of success in the future. It is likely that a predominant fraction of the in-use vehicle fleet from now through the 2020-2030 timeframe will be a combination of conventional vehicles and HEVs. More advanced technology vehicles, such as PHEVs, FCVs, and BEVs will likely not begin to significantly penetrate the market for new vehicle sales until the 2020 or later timeframe. Even under the most aggressively optimistic scenarios for the penetration of advanced vehicle technologies, where they would represent 87% of the entire fleet by 2050, these advanced technologies are expected to represent at most 25% of the in-use fleet by 2030. Irregardless of how optimistic these estimates are on the development and implementation of advanced electric/battery/hydrogen technologies, it is evident that liquid fuels will remain the predominant fuels for at least the next 30 years. Thus, funding resources for this time period should be allocated towards technologies and fuels that will produce renewable liquid-based fuels with low carbon intensities that can be produced within the State. This would include ethanol, other alcohols such as methanol and butanol, renewable diesel, such as biodiesel, Fischer-Tropsch diesel, or hydrogenated renewable diesel, or synthetic gasoline. Fuels such as CNG, LPG, hydrogen, DME would all require the introduction of specialized vehicles and fueling infrastructure that will not likely be feasible over the next 10-15 years with the exception of commercial fleets. Thus, our recommendation is that the development of these fuels not be ignored but, from a pragmatic point of view, have a lower priority for research funding in the near-term.

Feedstock Availability

The availability of feedstock in California will be another important driving factor in evaluating the technologies/fuels that will have the highest probability of success. From the results of previous studies, the distribution of potential feedstocks within the State will likely be regionally dependent. Forestry residues will likely be the predominant source in northern California. Agriculture biomass will be more prominent in the central part of the State. In urban areas and in the southern California area, municipal solid waste will likely be the most readily available

feedstock source. Other feedstock sources such as algae or drought-tolerant energy crops may have a broader distribution within various parts of the state. In addition to the broader regional questions with respect to feedstock, it is also important to understand the concentration of feedstock that might be available within a reasonable transport distance to a production facility. While regional studies of potential feedstocks within California have been performed, there have been few/no studies of the optimal locations for facilities that would provide the greatest concentration of feedstock within a reasonable transportation distance. The local potential for various biomass feedstocks will be a critical factor in determining if production facilities can be cost effective at various locations. Given the critical nature of this question, a study to characterize the local potential of various biomass feedstocks should be one of the highest research priorities, since this information will be central to determining what production technologies would be viable.

Environmental Issues

Environmental issues, such as greenhouse gas reductions and improvements in air quality, are some of the most important driving factors for the development of alternative fuels. Since environmental factors are critical to the promotion of alternative fuels, it is important to evaluate the environmental benefits/liabilities of various alternative fuels as they continue to be developed.

Some important methodologies in evaluating environmental impacts of various fuels are well-to-wheel and biomass production-to-wheel models. Although such models are being developed, their results are very dependent on the inputs. As such, these models should be reviewed by an independent body, that their inputs be scrutinized, and that the model outputs should be verified by experimental measurements. It is also worth noting that CARB has not done well-to-wheel evaluations for thermochemical processes to date. The allocation of some PIER funds towards such analyses could be beneficial in determining how PIER funds should be distributed between thermochemical and biochemical processes. In California, all new fuels being brought into the marketplace must also undergo a comprehensive multimedia evaluation of any potential significant adverse impacts the fuel may have on public health or the environment, including air, water, or soil, that may result from the production, use, or disposal. This process is extensive and costly and could impact the ability to implement new fuels. While worth mentioning, the funding of such multimedia evaluations is beyond the scope of PIER's efforts, since fuels undergoing multimedia evaluation are typically relatively near the point of commercialization.

Developing Biorefineries that can Process Feedstocks in a Comprehensive Way

In developing a long term future for fuel production, it is important to develop facilities that will process the feedstock in a comprehensive way, i.e. convert the maximum amount of feedstock to viable products, produce the minimum amount of waste, and the minimum amount of pollution. In this way, such fuel production facilities would be comprehensive biorefineries. This would include the processing of residual components to produce heat or energy that will meet a portion of the overall system requirements. The viability of such facilities could be evaluated with comprehensive process economic models.

Ethanol and Biobutanol from Corn and Sugarcane

Ethanol from corn is the most widely used alternative fuel in the US. Ethanol production is predominantly from starch- or sugar-based feedstocks such as corn (starch-based) in the US or sugarcane (sugar-based) in Brazil. The main limitations for this technology is the availability of feedstocks and regulatory limits on the amount of ethanol that can be used in gasoline.

Biobutanol has not been commercialized as yet, but is included in this chapter because it can be produced by modifications of the processes to produce ethanol and has some advantages over ethanol.

Status of Technology Development

- **Ethanol Production:** Ethanol production from corn and sugarcane technologies is a mature commercialized technology. The leading corn ethanol producers in the US are POET, LLC (formerly Broin), Archer Daniels Midland Co. (ADM), and Valero Renewable Fuels, LLC. The collective nameplate capacity of corn ethanol production facilities installed in the United States exceeded 13,000 MGY, with operating production greater than 11,800 MGY, as of January 2010. Even at 2009 levels, however, when about one-third of the U.S. corn crop went to ethanol production, this represented only 8% of the use of gasoline in the country on a volumetric basis, and an even lower percentage on a energy basis.
- **Butanol Production:** Biobutanol production has not been commercialized. One current method for biobutanol production involves fermenting corn starch using genetically modified yeasts. This basically involves modifying an ethanol production plant to make it a biobutanol production plant. If all ethanol plants were converted to biobutanol plants slightly more gasoline might be replaced, but it would not be significant relative to the US demand for gasoline.

Technological and Commercialization Gaps

- **Feedstock Limitations:** Concern regarding the use of land and crops that could be used for human or animal food consumption will limit the extent to which starch or sugar-based ethanol production can expand.
- **Increase blend limits:** The growth of the conventional ethanol industry is currently limited by consumer demand and allowable 10% regulatory blend limits into conventional gasoline.
- **Production Maturity:** Since ethanol production from starch- or sugar-based feedstocks is a mature and commercial process, it is not expected that there are any significant advances in production that will dramatically improve the commercialization prospects of conventional ethanol production.
- **Utilization Issues:** While ethanol is already used extensively in blending with gasoline, there are a number of issues with the utilization of ethanol within the traditional petroleum infrastructure and with conventional gasoline vehicles. An important limitation is that ethanol cannot be utilized in traditional pipelines. Another limitation is the low

energy density of ethanol compared to gasoline, and the corresponding reductions in fuel economy associated with this.

Potential Research Areas for Funding

- **Investigate most cost effective biobutanol production:** Biobutanol has some obvious advantages over ethanol and it has been shown that current ethanol facilities can be modified to produce biobutanol. The advantages of butanol include its better compatibility with the petroleum infrastructure and vehicles and its higher volumetric energy content. Investing in determining the most cost effective method to produce biobutanol, whether by modifying existing ethanol facilities or building facilities from the ground up is justified.
- **Develop variations of sugarcane and other sugar-rich feedstocks:** Variations of sugarcane and other sugar-rich feedstocks that are suited for rapid growth in colder and drier climates are needed if these are to be considered for growing and processing in the US. It does not appear that such research would provide any significant breakthroughs that would facilitate further commercialization of conventional ethanol as a transportation fuel.
- **Investigate biomass-powered combined heat and power at existing ethanol facilities:** It is likely that the suppliers of corn for the production of ethanol would also be able to supply corn stover or other agricultural residues that may be able to displace at least a portion of the fossil fuel requirements of the typical ethanol production facility. This could reduce the greenhouse gas (GHG) footprint of the facility. However, such research would probably not provide significant breakthroughs that would facilitate further commercialization of conventional ethanol as a transportation fuel.
- **Vehicle Compatibility:** From a research standpoint, one of the most important priorities in this area should be investigations of the compatibility of higher alcohol/gasoline or higher alcohol/ethanol/gasoline blends with vehicle hardware and the effect on emissions. This could allow higher alcohol or higher alcohol/ethanol levels in gasoline, which would also be beneficial for the expansion of cellulosic ethanol. This research area is listed here for completeness, but this area is beyond the scope of topics covered under funding by the Alternative Fuel section of the PIER-Transportation Research Area. Such research would be more appropriately funded under the Vehicle Technologies section of the PIER-Transportation Research Area, or another outside agency or organization.

Research Recommendations

- It is unlikely that the production of starch- or sugar-based alcohols for fuel will expand significantly beyond current levels. Hence, it is not recommended that funds be allocated towards research for this technology unless this research could also facilitate the commercialization of another more promising technology. The development of biomass-powered combined heat and power technologies would probably be the research that would be most applicable to other technologies.

Biodiesel

Biodiesel is the second most prevalent alternative fuel in the US. Biodiesel use has grown considerably over the last 10 years and the industry has reached some level of maturity. The important issues with expanding biodiesel use in California appear to be increased use of biodiesel and feedstock availability.

Status of Technology Development

- **Process Maturity:** The FAME biodiesel production process is fully mature and well understood. Biodiesel has expanded considerably in the past decade. The actual estimated US Biodiesel production by fiscal year (Oct 1 – Sept 30) for 2008 was 700 million gallons, up from only 2 million gallons for 2000.

Technological and Commercialization Gaps

- **Increased NO_x Emissions:** Biodiesel addition to diesel fuel is known to increase NO_x emissions. This is an important issue in California, since any changes in fuel regulations or fuel formulations must be done in a way that will not cause any increases or “back sliding” of any emission component.
- **Feedstock Limitations:** Currently, soybeans are the major feedstock for biodiesel production. Similar to ethanol, the use of soybeans for fuel production provides some competition for food uses. Soybeans also have many other uses and if the farmers can sell their soybeans at a higher price for these other uses then the biodiesel producer may not be able to get the supply they need. If all of the soybean oil, recycled restaurant grease, and other associated feedstocks were used to produce biodiesel, ~1.7 billion gallons of biodiesel could be produced each year, which is only ~5% of the current US on-road diesel usage.
- **Utilization Issues:** From a utilization standpoint, there are some issues with the use of biodiesel, including long term durability of systems with biodiesel, engine warranties, fuel quality, storage stability, and cold weather operability. While these issues are considerations with the use of biodiesel, they will probably not be the most significant issues for further commercialization prospects of biodiesel.

Potential Research Areas for Funding

- **Development of NO_x Mitigation Strategies:** In California, the mitigation of NO_x emissions from FAME biodiesel blends is an important issue. The development of more cost effective fuel formulations for NO_x reduction would be an important help for biodiesel economics. This could include more effective additives or combinations of biodiesel feedstocks that are less prone to increasing NO_x emissions.
- **Find low cost feedstocks:** A low cost feedstock which doesn't have significant other uses would help to stabilize biodiesel supply. Jatropha, which is a bush of little commercial importance that can be grown on marginal lands, is one possible new candidate feedstock. The development of new feedstocks for oils would also facilitate the expansion of the hydrogenated vegetable oil process as well.
- **Determine the properties of any new potential feedstocks:** The properties of any new feedstocks need to be characterized with respect to impurities, the need for pretreatment

as part of the production process and any associated waste products, the properties of the biodiesel produced, and the emissions when the biodiesel is used in an engine.

Research Recommendations

- Similar to starch- or sugar-based alcohols, it is unlikely that the production of FAME biodiesel will expand significantly beyond current levels, and it is not recommended that funds be allocated towards research for this technology unless this research could also facilitate the commercialization of another more promising technology. The development of low cost feedstocks, such as jatropha, would probably be the research that would be most applicable to other technologies.

Biochemical-Based Cellulosic Ethanol

Cellulosic biomass is expected to be the most significant source for production of ethanol, and other alternative fuels going into the next decade, in response to legislative initiatives. While cellulosic ethanol can be produced from a variety of different feedstocks, including agricultural residues, forestry and mill residues, municipal solid waste, and energy crops, it is more difficult and costly to produce cellulosic ethanol compared to converting sugars or starches to ethanol.

Status of Technology Development

- **Process Maturity:** Commercial ethanol production from cellulosic biomass is not available in the US yet. Several companies, including Abengoa Bioenergy, Iogen, BlueFire Ethanol, Mascoma, and POET, are working to develop commercial-scale biochemical ethanol production facilities. There are also a significant number of private companies developing and optimizing the enzymes and microorganisms necessary for biochemical production of ethanol from cellulosic feedstocks.

Technological and Commercialization Gaps

- **Production Costs:** The most significant technical barrier to the commercialization of these biochemical facilities is the lack of efficient and economical cellulose pre-treatment and enzymatic hydrolysis processes. Pretreatment is the most expensive operation within the production process. Cellulase enzymes and enzymatic hydrolysis are the second most costly element of the production process.
- **Utilization Issues:** As discussed above, ethanol has a number of limitations in terms of utilization, including a blend limit of 10% for conventional gasoline, the inability to use ethanol in pipelines, and its lower energy density.

Potential Research Areas for Funding

- **Reduce production costs:** Cost reductions are needed in harvesting, handling, storage, preprocessing, and processing.
 - Pretreatment is the most critical area within the production process. Continued advances are needed in pretreatment technologies to improve sugar yields, reduce the chemical and energy requirements of the process, and minimize the production of inhibitory byproducts. A better understanding of the factors that promote the

- resistance to microbial destruction, or recalcitrance, in the biomass feedstocks is also needed to identify critical pathways in improving process cost effectiveness.
- Enzymes with better reaction rates, or specific activities, are needed to achieve high conversions with much less enzyme. Enzyme mixtures that can effectively release the hemicelluloses left in pretreated solids are also important for achieving the high yields needed for large-scale competitiveness.
 - Consolidated Bioprocessing can be used to incorporate enzyme production, hydrolysis, and fermentation into a single process step. More extensive process integration research can be utilized to generate integrated performance data and develop predictive mathematical models that can guide process optimization and scale-up. Research in process integration can require large or multidisciplinary teams and correspondingly larger program budgets.
 - PIER should coordinate funding in this area with the already on-going work that is being funded by the US DOE. This would emphasize the study of unique processing requirements for California specific feedstocks including:
 - Develop and understand the pretreatment and resultant degradation for the specific feedstocks.
 - Fundamentals of cell walls of these materials.
 - Understand the unique enzymatic requirements for the hydrolysis of the pretreated product.
 - Optimize the integrated process of pretreatment, enzyme production, enzymatic hydrolysis, and fermentation for these feedstocks.
 - **Develop improved feedstocks:** There is a need for high yielding and faster growing feedstocks which are drought resistant, have higher carbohydrate content, reduced fertilizer demand, and are less recalcitrance to biochemical conversion.
 - The DOE is very involved in funding cellulosic ethanol feedstock work. California should concentrate its research dollars on feedstocks that can be grown under the semi-arid and other climates found in California. PIER has an ongoing program with the California Department of Food and Agriculture to identify and evaluate food crops that can help identify California-based feedstocks suitable for further research.
 - **Understanding overall sustainability and environmental impacts:** Understanding the overall sustainability and environmental impacts of energy crop production at the watershed level is another important area of research. The DOE recently issued a funding opportunity announcement to study this issue. Energy crop production encompasses crops planted exclusively for energy production and natural forest growth. PIER should pay close attention to these studies in case there is the opportunity to leverage them towards cellulosic stocks native to California, or to crops expected to do well in marginal soils in California.
 - **Vehicle Compatibility:** As discussed above, for ethanol use to expand to higher levels in conventional gasoline, the compatibility of higher alcohol/gasoline or higher alcohol/ethanol/gasoline blends with vehicle hardware and the effect on emissions must be investigated. Research in this area would be outside the scope of topics that would be funded by the Alternative Fuel section of the PIER-Transportation Research Area, and as such would be more appropriate for funding under the Vehicle Technologies section of the PIER-Transportation Research Area, or another outside agency or organization.

Research Recommendations

- It appears that cellulosic ethanol will play an important role in the expansion of alternative fuels over the next 10 years and can utilize a broad range of feedstocks. As such, this is an area that PIER should allocate research funds to. Reducing production costs and developing improved feedstocks should be the highest priorities for research. As this technology is being funded extensively at the Federal level and in the private sector, PIER funds should be targeted toward development of feedstocks that would be most applicable for California and how to optimize the production processes for these feedstocks.

Thermochemical to Liquid

Gasification is a thermochemical production technique that can be used to produce a range of different fuels for transportation. The synthesis gas from gasification can be utilized for the production of diesel fuel via a Fischer-Tropsch (FT) process, ethanol via catalysis or fermentation, methanol, DME, or “green gasoline” from a methanol intermediate. The primary advantage of gasification is that it can utilize a very wide range of feedstocks compared to other processes. The disadvantages of gasification are that it is a complex and expensive process and that it is energy intensive.

Status of Technology Development

- **Biomass to Fischer Tropsch liquids:** There are a few projects either in-place or being developed for producing FT fuels from biomass. The companies developing or proposing biomass to FT facilities are Oxford Catalysts, Rentech, Flambeau River/NewPage, Stora Enso/Neste Oil, and FZK.
- **Thermochemical Processes for Ethanol Production:** A small number of facilities are believed to be under construction, but there are no commercial thermochemical cellulosic ethanol facilities currently in operation in the United States.
- **Methanol, Dimethyl Ether, and Methanol to Gasoline (MTG):** The production of methanol from syngas is a well understood, commercial process. The MTG technology is fairly mature. In the United States, there have been proposals to develop MTG facilities. Commercial coal gasification to methanol, DME, and MTG projects have recently begun operation in China. There are no commercial biomass gasification to methanol or gasoline via the MTG process being developed.
- **Jet Fuel:** The increased costs the airlines expect to see from the regulation of CO₂ emissions have driven the industry to put the production of jet fuel from renewable biomass on a fast track. Gasification followed by Fischer-Tropsch processing is one of the technologies being developed for renewable jet fuel production.

Technological and Commercialization Gaps

- **Economies of Scale:** Biomass to FT units will be constrained by the scale of biomass feedstock availability. The higher BTU content of coal and coke, along with the large-scale availability of these feedstocks, allows FT units based on these inputs to be built approximately 10 times larger and more economically.

- **Process Specific Reactors:** Most FT reactor focus has been on large-scale coal and natural gas based systems. Because of this, many vendors do not have offerings at the scale needed for biomass and have not spent time and effort developing an optimized reactor for this smaller system.
- **Scale-Up:** As with most developing technologies, issues tend to arise that are not accounted for when moving from the demonstration or pilot scale to commercial operation.
- **Catalyst Shortfalls:** Most improvements in FT catalysts in the last 80 years have been largely incremental and most research has focused on coal-based syngas. Developing catalysts with higher per pass conversion, better selectivity, and lower sensitivity to impurities would improve the overall process economics.
- **Biomass Quality:** Building a large biomass to FT plant will require obtaining feedstock from different sources, each of which may vary in size and composition. This variation can cause gasification problems and require significant pre-processing, adding to the overall system costs. The preprocessing requirement for some fuels, such as renewable jet fuel, may require even greater levels of processing due to the more stringent requirements on the final fuel.
- **Impurities and Gas Cleaning:** Due to the specific requirements of current FT catalysts, syngas must be cleaned to very tight specifications. The most pressing issues are tar removal and clean-up temperatures. Many tar removal technologies are either ineffective or very detrimental to process efficiency. Many gas clean-up processes also require cooling the syngas from gasifiers exit temperatures to near 100 °F before reheating the syngas back to 500 °F for feed to the FT unit.

Potential Research Areas for Funding

- **Economies of Scale:** There is a need to develop much smaller gasification/FT units that can be operated economically, since the available biomass within a reasonable transportation distance cannot support the large units designed for natural gas or coal.
- **Scale up: Demonstration and pilot scale units need to be developed to explore issues which** may arise when designing and operating a commercial size unit.
- **Biomass Quality:** Pretreatment processing of the biomass prior to gasification may be an option for producing a more uniform product for the gasifier. The impact of pretreatment of biomass feedstocks on the subsequent gasification processing could be evaluated.
- **Selective FT Catalyst:** There is a need to develop FT catalysts with higher per pass conversion, lower sensitivity to impurities and/or process conditions, and better selectivity for carbon number, which dictates the type of products produced (the split between gasoline, jet, and diesel boiling range compounds). Meeting these objectives would require the successful manipulation of the FT chain-growth mechanism, which has not been achieved as of yet. Monolithic and edge coated FT catalysts are being investigated for selective FT synthesis.
- **FT Process Intensification:** Process intensification is the consolidation of multiple process steps into a fewer number of units. This helps to improve efficiency and lower overall costs. Options include development of economic reactor technologies for syngas conversion based on process intensification, catalyst/reactor integration, and heat management to improve the viability of biomass-based FT systems. Development of

modular-type reactor systems could help improve the viability of distributed biomass gasification plants.

- **High Temperature CO₂ and Sulfur Removal:** Syngas produced from biomass conversion includes a large fraction of CO₂ and may include some amount of sulfur. The presence of CO₂ can have detrimental effects on syngas conversion, and even small amounts of sulfur can be poisonous to FT catalysts. High temperature CO₂ removal using advanced sorbents or membranes could improve the process efficiency by reducing the cooling and reheating requirements. High temperature sulfur removal has been demonstrated using circulating beds of solid sorbents. None of these technologies are commercially available.
- **Tar Removal:** Tar production during the gasification process is another contaminant which must be removed prior to the FT unit and better methods for this removal are needed.
- **Catalytic Biomass Gasification:** In addition to traditional noncatalytic gasification processes, catalytic gasification of biomass can be used to lower the operating temperature, making the process more economically feasible. Rapid deactivation by tar formation at the lower temperatures of catalytic gasification has led to the search for more tar-resistant, but still active, gasification catalysts.
- **Steam Hydrogasification Reactor (SHR):** Hydrogasification combines a SHR with a Steam Methane Reformer (SMR) to produce a syngas for Fischer-Tropsch processing. Since the process does not require oxygen, which is very expensive, or air, which significantly decreases the calorific value of the product gases because of the high nitrogen content, SHR may be more economical to produce at a smaller scale. Also, because SHR uses a wet feedstock, there is no need for pretreatment to dry the feedstock.
- **Feedstocks:** Similar to the recommendation made for cellulosic ethanol it is recommended that California concentrate its Fischer-Tropsch efforts on California feedstocks.
- **Market Conditions:** Specific market conditions would also be helpful in making this type of project economic. Having low or negatively priced feedstock (i.e., with a tipping fee) would be helpful to make biomass FT projects attractive. Integrating the processing and upgrading for a FT process with an established refiner may reduce capital and operating costs. Co-firing of Biomass with coal or petcoke would reduce the environmental impact relative to straight fossil fuel feedstocks while taking advantage of the economy of scale that comes with a fossil based facility. Taking these three factors into account, it appears that locating a biomass to FT facility near a large metropolitan area and using urban wood wastes could be the most economic arrangement for a biomass to FT facility.

Research Recommendations

- The development of thermochemical processes could play a key role in optimizing the production of fuels for transportation. Thermochemical processes can utilize a wider range of feedstocks compared to biochemical processes and can also be integrated into processes for combined heat and power. This includes applications such as renewable jet fuel, which is beginning to attract interest from the public and private sectors. Synthetic alternative fuels produced from thermochemical processes

can also provide liquid fuels that would be very compatible with the anticipated vehicle technology mix going out at least 20 to 30 years into the future. Given these considerations, it is recommended that PIER allocate funds toward research efforts in gasification or other thermochemical technologies. Gasification processes tend to be larger in scale and more complex compared to other technologies, hence the viability of gasification processes may hinge on having a sufficient supply of feedstock within a reasonable transport distance of the facility. Thus, it will be important to determine if optimal locations can be found within the State that provide a sufficient quantity of feedstock within a reasonable transport distance, as discussed above. If such locations can be identified, then further research into improving gasification production technology could be of merit. Alternatively, technologies that can be built at a smaller scale, such as hydrogasification, may merit further research and development.

Pyrolysis

Pyrolysis is another thermochemical process that can be used to convert biomass from a wide range of sources to a liquid fuel. Pyrolysis differs from other thermochemical processes in that it is done in the absence of oxygen and at lower temperatures. The resulting pyrolysis oil is a fairly low quality product that requires considerable upgrading to meet transportation fuel quality specifications.

Status of Technology Development

- While there have been limited niche successes, there has been no widespread commercialization of pyrolysis as yet. There are four companies that appear to be most heavily engaged in commercialization efforts today: Dynamotive, Ensyn/Envergent, BTG, and PyTec, with Dynamotive being the most active. Upgrading pyrolysis oil to high-quality hydrocarbon fuels has been demonstrated at a non-commercial scale.

Technological and Commercialization Gaps

- **Pyrolysis Oil Quality:** The quality of raw pyrolysis oil is very poor, requiring extensive upgrading before it can be used as an on-road transportation fuel. While technologies exist to do this, the high cost and low yield have typically made conventional options too expensive.
- **Small Sizes:** A large-scale pyrolysis oil plant of 100,000 tons (roughly 2200 barrels per day) is equivalent to 0.5 to 2% of the input to a typical crude oil refinery. Refiners will likely be reluctant to make major changes to their process to accommodate such a small amount of feedstock. In addition, new refinery applications (such as hydrocracking and hydrotreating) are typically built in the 10,000 barrel per day range or higher due to economies of scale.
- **Lack of Integration with Petroleum Refiners:** The most logical route for upgrading bio-oils would be partnership with petroleum refiners. Partnerships such as those that some oil companies have established for the production of other biofuel routes would be useful, such as BP (with Verenium), Shell (previously in a partnership with Choren, now dissolved), and ExxonMobil (with Synthetic Genomics).

Potential Research Areas for Funding

- **Improve knowledge of complex pyrolysis reactions:** Fundamental studies of the complex reactions are required to develop a unified theory to predict pyrolysis behavior for different feedstocks.
- **Catalytic (in-situ) pyrolysis:** Noncatalytic pyrolysis does not produce fungible gasoline and diesel products that can be used in the transportation infrastructure. When catalysts are used in pyrolysis, alkylation, isomerization and reforming reactions can take place to produce alkanes and aromatic and cyclic compounds, major components of diesel and jet fuel.
- **Improve upgrade catalyst formulations and reduce hydrogen requirements:** The petroleum refining industry continues to look at ways to develop and improve upgrading catalysts, which are catalysts designed to upgrade lower quality materials into higher quality products. These improvements could include higher yields and/or greater tolerance of poor quality feedstocks. Future research in this area, not necessarily related to pyrolysis oils, could be of benefit to the commercialization of this technology.
- **Upgrading bio-oil using syngas derived from biomass gasification:** To operate a stand-alone pyrolysis plant, it may be necessary to build a small gasifier to supply syngas to the adjacent pyrolyzer to achieve self-sustained operation. Using syngas as a hydrogen source for bio-oil hydrotreating has not been explored and the interactions between CO and bio oils needs to be better understood.
- **Enhancing the feedstock flexibility of pyrolysis units:** Improving reactor performance to allow a wider range of feedstock types and reducing sensitivity to size and content would lower the cost of raw materials and improve yield.
- **Effect of alkaline cations in biomass feedstock:** There is a need for a more systematic understanding of the role of different alkaline cations, as well as the alkaline cation concentration, on the pyrolysis reaction. The introduction of different catalytic materials could be used to alter the product bio-oil composition.
- **Continue research on novel upgrading strategies, such as microwave-activated pyrolysis:** More novel upgrading methods have the potential to make major step changes in the cost or equipment required to perform upgrading. Microwave-activated pyrolysis is an example of one such technology.
- **Medium scale conversion systems:** Pyrolysis seems to offer a potentially attractive scale match for medium scale conversion systems (e.g., 50 to 250 tons/day) that could be deployed in a distributed strategy for storable liquid fuel production. This could address some fundamental drawbacks with long-distance transport of typically bulky biomass feedstocks to large centralized biomass conversion facilities.

Research Recommendations

- Pyrolysis is part of the suite of thermochemical technologies that PIER should allocate research funds towards. The smaller-scale, less expensive nature of pyrolysis in comparison to other thermochemical processes provides useful advantages that help offset the poor quality of the pyrolysis oils that are produced. The potential of utilizing pyrolysis to “densify” raw biomass to pyrolysis oil at distributed, remote locations, which can subsequently be transported to a centralized processing/upgrading conversion facility,

appears to merit further investigation. Economic analyses of the viability of such a strategy could be tied to the study recommended above on identifying optimal facility locations based on feedstock distribution. The upgrading of product oils to transportation-quality liquid fuels is the most significant technical challenge for pyrolysis and it is suggested that this be the primary emphasis of any pyrolysis research funding. The petroleum industry continues to look at ways to develop upgrading catalysts that can improve yields and be more tolerant of poor quality feedstocks. Some strategies that could be used to facilitate upgrading include utilizing syngas from a small gasifier, in-situ catalytic pyrolysis, or the development of more novel upgrading methods, such as microwave techniques.

Renewable Diesel

The hydrogenation of vegetable oils and animal fats uses more traditional refining methods of hydrotreating to produce diesel fuel. The finished product is similar to traditional diesel, with a hydrocarbon mixture of isoparaffins and paraffins, which is compatible with the traditional pipeline, fueling, and vehicle infrastructure.

Status of Technology Development

- There are currently several facilities producing renewable diesel fuels on a commercial basis around the world. The process has been commercialized in Europe, where the economics are more favorable, but not in the US as of yet. Neste Oil has one of the most advanced renewable diesel programs, with two existing facilities in Finland and two more facilities in Singapore and Rotterdam, respectively, being built. Other companies working on the development of renewable diesel include ConocoPhillips, BP, UOP, Petrobras in Brazil, Nippon Oil, and CanmetENERGY.
- **Jet Fuel:** Hydrotreating Vegetable Oils in another technology being developed for the production of renewable jet fuel that has been the subject of a number of projects backed by the airline industry or government entities.

Technological and Commercialization Gaps

- The use of the technology will be driven largely by the economics of the process, including the cost of vegetable oils and animal fats, if they are available in sufficient quantities to sustain a continuously operating process, the cost/availability of hydrogen, and the capital required to develop a vegetable oil and/or animal fat hydrotreater as a standalone facility or at an existing petroleum refinery.

Potential Research Areas for Funding

- **Feedstock Availability and Cost:** The development of lower cost feedstocks, similar to those suggested for FAME biodiesel, is an important area of research. Such research would be useful for the development of the biodiesel market as well.
- **Co-processing vegetable oils and/or animal fats with diesel fractions:** A lower capital cost option would potentially be the hydrotreating of vegetable oils and/or animal fats with diesel fractions simultaneously. This would likely take place within an existing petroleum refinery and require modifications to the existing diesel unit. This strategy

would also likely reduce the life of the hydrotreating catalyst if pre-treatment of the vegetable oils and/or animal fats is not performed. Research focus on hydrotreating catalysts that can handle blends of petroleum fractions and vegetable oil and/or animal fat at the same time may be of interest.

- **Improved catalysts:** Whether the vegetable oil or animal fat is hydrogenated in a separate unit or co-processed with the diesel fractions, the activity, stability, and useful life of the catalysts needs to be improved.
- **Understanding contaminant impacts on production:** Understanding the influence of contaminants in the processing and controlling issues such as corrosion could help in improving the production process.

Research Recommendations

- Hydrotreating has the advantage of being a well developed refining process that produces a fuel that has properties of a high quality diesel or jet fuel. While some of the research recommendations for renewable diesel are unique to hydrotreating vegetable oils, so of the other suggestions would have applications towards other technologies as well. The development of feedstocks applicable to renewable diesel could similarly be used in the production of other fuels, such as biodiesel. The development of the ability to co-process vegetable oils and/or animal fats would also potentially facilitate the co-processing of other feedstocks such as pyrolysis oils. Similarly, improving the activity, stability, and useful life of catalysts for vegetable oils, would probably also provide benefits for the processing of either traditional petroleum streams or other biomass-related materials. Given the emphasis on upgrading processes and feedstock development, it is recommended that PIER funds also be allocated toward the development of renewable diesel and its associated feedstocks.

Algae

Algae-based fuels have many promising characteristics. Algae can provide much higher oil yields than more traditional terrestrial crops such as soybeans or palm oils. Algae can be grown in a variety of aqueous environments, including in water sources on marginal lands unsuitable for food crops. Thus, algae do not compete directly with food supplies. Interest and investment in algae-based fuels is rapidly growing. Although much research is still needed to make algae-based fuels a viable transportation substitute, algae-based fuels could represent the next generation of fuels that follow those derived from cellulosic ethanol.

Status of Technology Development

- Currently, there are no commercial algae production facilities because research has not yet demonstrated a viable production method that can be sustained on a continuous basis, as toxic by-products interrupt the algae growth. Considerable basic and applied R&D is needed to overcome the current technical barriers for algal-based fuel production and the cost effective production of algae is a good 10 years away. Nevertheless, investment in the development of algae-based fuels is expanding in both the private and government sectors. ExxonMobil, in collaboration with Synthetic Genomics Inc., and Chevron, in collaboration with Solazyme, are both working on the development of algae-based fuels.

The US DOE and NREL have a number of algae research projects underway, and a National Advanced Biofuels Consortium has just been funded to be led by NREL and the Pacific Northwest National Laboratory. A number of small venture companies are also active, with Algenol Biofuels Inc., Solazyme Inc., Sapphire Energy, and Univenture and Algaeventure all receiving funding from the Federal government to develop pilot plants or develop new production methods. Algae is also being developed as a potential feedstock for the production of renewable jet fuel.

Technological and Commercialization Gaps

- **Stability of large scale cultures:** Ideally, one wants to grow a specific algal strain that is known to be a good source for fuel production. This can be difficult to accomplish, particularly in an open pond system, because of contamination with algal strains native to the area, or predators and/or pathogens, which could be destructive to a specific algal strain.
- **Nutrient sustainability and management:** Algae require a sustainable supply of low cost nutrients to achieve rapid growth. On the other hand, some nutrients need to be restricted to increase algal oil formation. Managing these tradeoffs to optimize fuel production is a key technical challenge.
- **Water management:** The cultivation of algae requires large quantities of water. To improve the overall production effectiveness, designs must be developed to conserve water and to optimize and control the water recycle. These systems must also monitor changes in water quality due to evaporation and properly treat entering and exiting water.
- **Harvesting, dewatering, extraction, fractionation, fuel production:** The costs of all of these steps must be reduced, some substantially, to make fuels from algae economic.

Potential Research Areas for Funding

- **Development and optimization of algae strains:**
 - **Developing stable, competitive production strains:** The strains need to be resistant to attack from pervasive algal predators and pathogens. This represents one of the most important areas of research for algae strains. Other possible options to improve algae culture's susceptibility to predator invasion include chemical treatments and environmental or physiological adaptations.
 - **Wider growing conditions:** The strains need to be able to grow at a high rate over a wider range of ambient temperatures. Optimizing strains of heterotrophic algae, or algae that are grown in the dark, would also allow for greater diversity in the conditions that could be used for algae for fuel production. Identification of species that can better utilize shorter wavelengths to grow would also improve cultivation, since algae growth rates are often limited by light penetration into the ponds and shorter wavelengths will have greater penetration depths. Strains that can provide good yields with reduced water and nutrient levels would also be useful.
 - **Basic research in multi-trophic, molecular-level algal ecology:** Some algae species may process the nutrients more efficiently, but not produce the desired concentrations of oils and lipids, while their waste products may be efficiently converted to oils and lipids by another species.

- **Higher percent of total biomass as oil:** The strains need to produce a higher concentration of the oils and lipids, which are the precursors that can be processed to produce a fuel. There have been some important advances in this area, so this is less important than research toward resistance to biological attack and nutrient requirements.
- **Faster growth, higher biological efficiency:** Strains need to be developed that have faster growth rates and greater biological efficiency. There have been some important advances in this area, so this is less important than resistance to biological attack and nutrient requirements.
- **Cultivation of Algae:**
 - **Better control of culture stability:** Understanding the health and composition of the ponds used for growing algae remains an important element. Automated biological and chemical monitoring should be incorporated into any research geared toward the cultivation of algae. The information obtained from such monitoring would also be useful in the early identification of invasive species, predators, pathogens, the optimization of the chemical treatment of the pond, and in understanding the pond speciation, ecology dynamics, and frequency of contamination events.
 - **Management of water and nutrient requirements:** The management of the supply and the use of nutrients in the growth process is an important aspect of cultivation. Research in optimizing the control of nutrient levels, finding inexpensive sources of nutrients, and developing strategies to recycle nutrients would all improve the production process. Managing the water demands for large cultivation systems is also important. Additional research in designing systems to conserve water, optimizing and controlling water recycle, treating entering and exiting water, and addressing changes in water quality due to evaporation would be useful in this regard.
- **Downstream processing of algae for major cost reductions:**
 - **Understanding the fundamental aspects of algae relating to downstream processing:** This would include research to understand the impacts of processing on cell wall composition. Studying and understanding lipid genesis, composition, and structure could also be useful in optimizing extraction yields.
 - **Developing improved systems for downstream processing:** The technologies for extracting algae are expensive in terms of either equipment costs or energy requirements. Systems or engineering improvements in these areas would improve the economic viability of algae production as a whole. This could include the development of multitasking extraction processes or improved methods for dealing with water in the downstream processes.
- **Use of algal residuals after the lipids or other desirable fuel precursors have been extracted:** This could include the processing of the residuals to provide energy to reduce the processing energy cost or the development of valuable co-products. This would help improve the overall economics of the processing. Gasification or thermochemical processing of the entire algae produced rather than making biodiesel based fuels should be investigated.

- **Lifecycle analysis of energy and carbon in selecting preferred fuel conversion technologies:** As for all alternative fuel production methods, lifecycle analysis of energy and carbon must be considered in selecting the optimum method for fuel production.
- **Integration issues and opportunities for algal cultivation facilities co-located with industrial CO₂ sources and/or wastewater treatment facilities:** Since wastewater and CO₂ can serve as the main nutrient sources for algae, co-locating the algae growing near these sources could substantially reduce the growing costs.

Research Recommendations

- Algae-based fuels may represent the next generation of biochemical based fuels that would follow those derived from cellulosic ethanol. The increase in funding at the Federal level and the number of companies (many based in California) becoming involved in the study and development of algae-based fuels is one important indicator of the optimism. It is recommended that research toward the development of algae-based fuels be supported by PIER as a medium term transportation fuel strategy, with implementation into the marketplace out 10-20 years. This could include research spread out among the different main areas for funding described above, including the development and optimization of algae strains, the cultivation of algae, or downstream processing or coprocessing of algae.

Other Technologies

A number of other technologies were reviewed that included more mature technologies, such as CNG and LPG, that are not likely to expand market share going into the future, and technologies that still require a significant research to become commercially viable, such as hydrogen and other technologies. The recommendations for these technologies are reviewed below.

Natural Gas/Anaerobic Digestion

Natural gas has been used in vehicle applications for several decades, but the vehicle availability and refueling infrastructure are still limited. Additionally, natural gas is currently produced from fossil fuel sources. For this roadmap the production of methane, the principal component in natural gas, from anaerobic digestion of organic matter was examined. This process occurs in landfills and is also used in wastewater treatment facilities, dairies, and animal feeding operations. Producing methane via anaerobic digestion has several limitations, including the poor quality of the gas and competition with the typical use for electricity/energy generation. Given these limitations, it was concluded that anaerobic digestion would not likely make a significant contribution towards alternative transportation fuels. Natural gas can also be produced via other biochemical or thermochemical processes or harvested from methane hydrates, but even for these other methods, the issues with vehicle availability and infrastructure would likely limit this technology to niche markets. Considering all of these factors, it is recommended that PIER funds not be allocated toward research in natural gas for transportation applications.

Liquefied Petroleum Gas (LPG)

LPG has similar limitations as natural gas with respect to vehicle availability, refueling infrastructure, and the fact that LPG is currently produced from fossil fuel sources. The development of LPG for transportation applications is less developed than that for natural gas vehicles (NGVs). Although there is some specific research into producing propane from biological sources, this research is still in its infancy and mostly being conducted at a university level. Also, many of the methods that would be used for the production of propane, can also be used to produce fuels that are more similar to gasoline and diesel fuel that could be used in existing vehicles and with the existing infrastructure. Based on the limitations with vehicles and infrastructure, and the lack of unique production advantages, it is recommended that PIER funds not be allocated toward LPG research for transportation applications.

Hydrogen

There are still critical barriers to the continued development of hydrogen as a transportation fuel and a majority of the goals in a recent 5 year collaboration between the DOE and major automobile manufacturers were not met. Nevertheless, it appears that hydrogen could play a role as a transportation fuel in the longer term, 2040 to 2050 timeframe. California is already investing in a hydrogen fuel infrastructure, and there is also some industry investment in vehicle technology. It appears unlikely that hydrogen will have a significant impact as a transportation fuel over the next 10-15 years. Overall, it is recommended that hydrogen be included in the portfolio of fuel technologies to be supported by PIER. Hydrogen should be considered a longer term transportation solution, targeting a time horizon in the 2030-2050 period. PIER should continue to monitor developments in hydrogen production techniques and vehicle technology. Key areas for PIER funding should include fuel cell technology and hydrogen production techniques, such as solar energy. The funding for development of hydrogen fuel production technologies is most appropriate within the fuels section of the PIER-Transportation Research Area, while the funding of fuel cell or hydrogen internal combustion engine related projects is more appropriate for funding under the vehicle technology section of the PIER-Transportation Research Area.

Carbon Dioxide Conversion to Hydrocarbons

This technology is based on the conversion of CO₂ to a series of hydrocarbons when it undergoes an electrocatalytic reaction inside a confined carbon micropore with noble metal nanoclusters. Research into this technology is being conducted at a small number of universities throughout the world. This research is in the very preliminary stages in terms of commercialization, and many more years of basic research are required to determine if any such method would be viable for advancement to the pilot stage. Overall, it appears that other technologies are more viable for the longer term 2050 timeframe, so this area is not recommended for PIER funding as a long term fuels technology. This area is more appropriate for Federal funding, with the potential for PIER to reexamine funding opportunities if significant breakthroughs are made in the technology.

Fuels from Sunlight Program

This is a recently initiated DOE program focusing on generating fuels directly from sunlight. The initial grant of \$122 million in funding was awarded to a team of researchers from the California Institute of Technology (Cal Tech), Lawrence Berkeley National Laboratory, as well as a number of other Universities. The goal of the center is to develop an integrated solar energy-to-chemical fuel conversion system and move this system from the bench-top discovery phase to a scale where it can be commercialized. Research will be directed toward developing the functional components necessary to assemble a complete artificial photosynthetic system, integrating those components into an operational solar fuel system, and developing strategies for scale-up from laboratory to commercial viability. While development is still needed in this area before it is commercially viable, it appears that there is good momentum at the Federal level to move this program forward. As such, it is recommended that PIER direct some of the funding for its long term development efforts to this area. Given the level of funding already being provided by the Federal government in this area, PIER should look for specific niches to fund/supplement within the overall portfolio of this program. This niche could be within the solar energy area, which would potentially also have broader implications towards hydrogen production and the development of hydrogen fuels as a long term transportation solution.

References

Aatola, H., Larmi, M., Sarjovaara, T., and Mikkonen, S. (2008) Hydrotreated Vegetable Oil (HVO) as Renewable Diesel Fuel; Trade-off between NO_x, Particulate Emission, and Fuel Consumption of a Heavy Engine. SAE Technical Paper No. 2008-01-2500.

Abengoa (2010) See <http://www.abengoabioenergy.com/corp/web/es/index.html>

Abengoa. (2009a) Abengoa Bioenergy Hybrid of Kansas, LLC (ABHK) *presented at the Kansas Wind and Renewable Energy Conference October 9, 2009.* http://www.kcc.state.ks.us/energy/kwrec_09/presentations/B1_Robb.pdf, 2009.

Abengoa (2009b) “*New Technologies – Current Projects – Integrated Biorefinery,*”. 2009. http://www.abengoabioenergy.com/corp/web/en/nuevas_tecnologias/proyectos/biorrefineria_integrada/index.html.

Accelergy (2010) http://www.accelergy.com/docs/USAF_Benchmark.pdf

Accelergy Website (2010) http://www.accelergy.com/docs/RELEASE_Accelergy_Vail.pdf.

Aden, A. (2009) Biofuels from Biomass: LCA Considerations, Presentation at the CRC Workshop on LCA of Biofuels, Argonne, IL, October.

Aden, A., et al. (2002) Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL/TP-510-32438.

Aden, A. and Foust, T. (2009) Technoeconomic Analysis of the Dilute Sulfuric Acid and Enzymatic Hydrolysis Process for the Conversion of Corn Stover to Ethanol. *Cellulose*, vol. 15, pp. 535-545.

AFAVDC (2010) DOE Alternative Fuel and Advanced Vehicle Data Center website. http://www.afdc.energy.gov/afdc/fuels/hydrogen_production.html.

AFAVDC (2009a) Alternative Fuels & Advanced Vehicles Data Center, Starch- and Sugar-based Ethanol Feedstocks. July 10, 2009. http://www1.eere.energy.gov/biomass/ethanol_yield_calculator.html.

AFAVDC (2009b) Alternative Fuels & Advanced Vehicles Data Center, Biobutanol Production http://www.afdc.energy.gov/afdc/fuels/emerging_biobutanol_production.html

AFAVDC, (2009c) Alternative Fuels & Advanced Vehicles Data Center, Biodiesel Production, http://www.afdc.energy.gov/afdc/fuels/biodiesel_production.html

AFAVDC (2009d) Alternative Fuels & Advanced Vehicles Data Center, Cellulosic Ethanol Feedstocks, http://www.afdc.energy.gov/afdc/ethanol/feedstocks_cellulosic.html

AFAVDC (2009e) Alternative Fuels & Advanced Vehicles Data Center, Alternative Fueling Stations, See <http://www.afdc.energy.gov/afdc/fuels/stations.html>.

Algaeventure Systems (2009)

http://www.algaevs.com/wp-content/uploads/2009/03/avs_harvester_tech_expl.pdf

Algenol (2010) <http://www.algenolbiofuels.com/>

Alleman, T.L., McCormick, R.L., Deutch, S. (2007) *2006 B100 Quality Survey Results*; NREL/TP-540-41549; National Renewable Energy Laboratory: Golden, CO, May; <http://www.nrel.gov/docs/fy07osti/41549.pdf>.

Alleman, T.L. and McCormick, R.L. (2008) *Results of the 2007 B100 Quality Survey*; NREL/TP-540-42787; National Renewable Energy Laboratory; Golden, CO, March; <http://www.nrel.gov/docs/fy08osti/42787.pdf>.

Alleman, T.L. and McCormick, R.L. (2009) *2008 B20 Survey Results*; NREL/PR-540-45184; National Renewable Energy Laboratory; Golden, CO, 2 February; <http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/45184.pdf>

Alleman, T. A., Fouts, L., McCormick, R. L. (2010) Analysis of Biodiesel Blend Samples Collected in the United States in 2008, NREL/TP-540-46592, March; <http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/46592.pdf>

AltAir Fuels (2010) 14 Airlines Sign Landmark MOU for Camelina---based Renewable Jet Fuel & Green Diesel. Press release. www.altairfuels.com.

AMI (2004) Beyond the Internal Combustion Engine – The Promise of methanol Fuel Cell Vehicles, American Methanol Institute.

Amyris (2010) <http://www.amyrisbiotech.com/>.

Arachchige, S. M., J. Brown, and K. J. Brewer. (2008) Photochemical Hydrogen Production From Water Using the New Photocatalyst $[(bpy)_2Ru(dpp)]_2RhBr_2(PF_6)_5$. *Journal of Photochemistry and Photobiology A: Chemistry* 197, pp. 13 - 17.

Aresta, M., Dibenedetto, A., Tommasi, I. (2003) Energy from Macro-Algae, Fuel Chemistry Division Preprints, 48(1), 261.

Aresta, M., Dibenedetto, A., Barberio, G. (2004) Utilization of Macro-Algae for Enhanced CO₂ Fixation and Energy Production, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 49 (1), 349.

ASTM (2010) D7566 – 10 – Standard Specification for Aviation Turbine Fuels Containing Synthesized Hydrocarbons.

ASTM (2009) D4054 – 09 – Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives.

ASTM (2007) D1655 – 06d – Standard Specification for Aviation Turbine Fuels.

Atsumi, S., Hanai, T., and Liao, J. C. (2008) *Non-Fermentative Pathways For Synthesis Of Branched-Chain Higher Alcohols as Biofuels*, Nature 06450 Vol 451|3.

Austin, A. (2010) Agave shows potential as biofuel feedstock, Biomass Magazine, Feb. Available at: http://www.biomassmagazine.com/article.jsp?article_id=3485.

Basha, S. A., Gopal K. R., and Jebaraj S. (2009) A Review On Biodiesel Production, Combustion, Emissions And Performance. Renewable and Sustainable Energy Reviews, no 13, pp. 1628–1634.

Becker, M. (2008) MSU Researchers Receive Grant to Study Algae as a Source of Biofuels. Montana State University News Service, November. <http://www.montana.edu/cpa/news/nwview.php?article=6502>

Benning, C. (2010) Identification of Factors Required For Oil Biosynthesis In Microalgae. Algal Biofuels Symposium 2010, La Jolla. Not published.

Bevill, K. (2009) "Brazil introduces restrictions for sugarcane production." Ethanol Producer Magazine. October. http://www.ethanolproducer.com/article.jsp?article_id=5993.

Biodiesel Handling and Use Guide, forth edition (2009) NREL/TP-540-43672, http://www.nrel.gov/vehiclesandfuels/npcf/feature_guidelines.html

Biofuels Digest (2009) ConocoPhillips kills green diesel partnership with Tyson, says reduced subsidy made project uneconomic. May by Jim Lane.

BioJet Corporation (2010) www.biojetcorp.com.

Biojet (2010) <http://www.biojetcorp.com/>

BIWG (2006) Bioenergy Interagency Working Group. "Bioenergy Action Plan for California, Joint Agency Report." CEC-600-2006-010, July.

Bloch, M. (2008) The many uses of soy. May 11. <http://www.greenlivingtips.com/articles/224/1/The-many-uses-of-soy.html>.

Blommel, P.G. and Cortright, R.D. (2008) Production of Conventional Liquid Fuels from Sugars, White paper, Virent Energy Systems, Inc., Madison, WI, August. http://www.virent.com/BioForming/Virent_Technology_Whitepaper.pdf

BlueFire Ethanol (2010) <http://bluefireethanol.com/>

BlueFire Ethanol (2009) "Department of Energy Increases Funding to \$81 M for Phase II of BlueFire Ethanol's Planned Fulton, MS Biorefinery," December, <http://bluefireethanol.com/pr/76/>.

Bluefuel Energy Website (2010) <http://www.bluefuelenergy.com/page37/page37.html>.

Bourg, H. (2006) "Future Prospective of DME." 23rd World Gas Conference, Amsterdam.

Bournay, L., D. Casanave, B. B. Delfort, G. Hillion, and J. A. Chodorge (2005) "New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants." *Catalysis Today* 106: 190–192.

Bourzac, K. (2007) "A New Biofuel: Propane." *Technology Review*, Published by MIT, Thursday, April 19.

BP and Dupont (2010) Biobutanol Fact Sheet.

http://www2.dupont.com/Production_Agriculture/en_US/assets/downloads/pdfs/BP_DuPont_Fact_Sheet_Biobutanol.pdf.

British Petroleum (2009) BP Statistical Review of World Energy 2009, <http://www.bp.com/productlanding.do?categoryId=6929&contentId=7044622st=cse>.

Brown, L.R. 2008. "Why Ethanol Production Will Drive World Food Prices Even Higher in 2008." January 24. http://www.earth-policy.org/index.php?plan_b_updates/2008/update69.

Brown, L. R. (2009) Plan B 4.0: Mobilizing to Save Civilization, Supporting Data, http://www.earthpolicy.org/index.php?books/pb4/pb4_data.

Budny, D. and P. Sotero. (2007) "Brazil Institute Special Report: The Global Dynamics of Biofuels." Brazil Institute of the Woodrow Wilson Center, http://www.wilsoncenter.org/topics/pubs/Brazil_SR_e3.pdf.

Bullis, K. (2009) "Making Diesel from CO₂ and Sunlight, A new program will develop novel approaches to renewable fuels." *Technology Review*, Published by MIT: Thursday, December 10.

Busby, D., et al. (2007) Yield and Production Costs for Three Potential Dedicated Energy Crops in Mississippi and Oklahoma Environments. <http://purl.umn.edu/34854>, Dept of Agricultural Economics, Mississippi State, MS-39762: Draft of paper prepared for Southern Agricultural Economics Association Annual Meeting, Mobile, Alabama, February.

Butamax Advanced Biofuels LLC. (2009) Biobutanol - A more advanced biofuel.

http://www.butamax.com/assets/pdf/biobutanol_a_more_advanced_biofuel.pdf

(accessed November 25).

Byrd, A. J., K. K. Pant, and R. B. Gupta (2008) "Hydrogen production from glycerol by reforming in supercritical water over Ru/Al₂O₃ catalyst." *Fuel* 87: 2956–2960.

Cackette, T. (2010) Reducing Vehicle Emissions to Meet Environmental Goals. Presentation at the 20th CRC On-Road Vehicle Emissions Workshop, March.

Caffrey, P. and Machiele, P. (1994) "In-Use Volatility Impact of Commingling Ethanol and Non-Ethanol Fuels," SAE Technical Paper No. 94065, SAE, Warrendale, PA.

California Attorney General (2009) http://ag.ca.gov/globalwarming/pdf/cilion_agreement.pdf (accessed October).

California Biomass Collaborative (2008) An Assessment of Biomass Resources in California, 2007 [Report]: Draft report for California Energy Commission, PIER-Energy-Related Environmental Research Program. Contract 500-01-016, published in March.

California Board of Equalization (2009) http://www.boe.ca.gov/sptaxprog/reports/MVF_10_Year_Report.pdf (accessed November 25).

California Department of Water Resources (2009), <http://www.water.ca.gov/landwateruse/anaglwu.cfm>.

California Ethanol and Power (2009) <http://www.californiaethanolpower.com/> (accessed November 25, 2009).

California Fuel Cell Partnership (2009) "Hydrogen and Fuel Cell Vehicle and Station Deployment Plan: A Strategy for Meeting the Challenge Ahead." February.

CalNGV News (2010) New Plant Shows Biomass Potential, January. http://www.cngvc.org/pdf/newsletters/CalNGVNews_011110.pdf

CALSTART (2006) A Compendium Hydrogen-Blend and Hydrogen Fueled Internal Combustion Engine Activities, Prepared for U.S. Department of Transportation, Federal Transit Administration. FTA-CA-26-7069-1.

Canakci, M., A. Monyem, and J. Van Gerpen (1999) "Accelerated Oxidation Processes in Biodiesel." Transaction of the American Society of Agricultural Engineers, VOL. 42(6): 1565-1572.

CanmetENERGY (2010) http://canmetenergy-canmetenergie.nrcan-rncan.gc.ca/eng/industrial_processes/industrial_energy_systems/publications/200866.html.

CARB (2010) LCFS lookup tables. http://www.arb.ca.gov/fuels/lcfs/121409lcfs_lutables.pdf.

CARB (2009a) Proposed Regulation to Implement the Low Carbon Fuel Standard. Volume I: Staff Report: Initial Statement of Reasons. <http://www.arb.ca.gov/regact/2009/lcfs09/lcfsisor1.pdf>.

CARB (2009b) “Detailed California-Modified GREET Pathways for Brazilian Sugarcane Ethanol: Average Brazilian Ethanol, With Mechanized Harvesting and Electricity Co-product Credit, With Electricity Co-product Credit”.

CARB (2009c) Detailed California-Modified GREET for Cellulosic Ethanol from Farmed Trees by Fermentation, February. CARB (2009d) Detailed California-Modified GREET Pathway for Cellulosic Ethanol from forest trees, February.

CARB (2008) “Aftermarket, Performance and Add-on Parts Regulations”, “Certification of Alternative Fuel Retrofit Systems”
<http://www.arb.ca.gov/msprog/aftermkt/altfuel/altfuel.htm>.

CARB (2003) Draft Attachment B: Public Hearing to Consider Adoption of a Proposed Regulation to Implement the Low Carbon Fuel Standard - Staff’s Suggested Modifications to the Original Proposal. http://www.arb.ca.gov/fuels/lcfs/lcfs_att_b_mod.pdf.

CARB (1999) “Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate, Report to the California Environmental Policy Council in Response to Executive Order D-5-99, Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline” UCRL-AR-135949 Volume 3.

CARB (1998) “Comparison of the effects of a fully-complying gasoline blend and a high RVP ethanol gasoline blend on exhaust and evaporative emissions”, *Draft*, California Air Resources Board, Sacramento, CA.

Carter, C., Rausser, G. and Smith, A. (2008) The Food Price Boom and Bust. www.agecon.ucdavis.edu/extension/update/articles/v12n2_2.pdf

Cassman, K., Holzfaster, R., Kristen, D, Sneller, T., and Tieszen, L. (2009) Biofuels, Water Resources and Climate Change: Solving the Sustainability Puzzle.
<http://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1006&context=researchcondev>.

CEC/CARB (2007) "California Energy Commission and California Air Resources Board State Alternative Fuels Plan. Joint Agency Report." CEC-600-2007-011, October.

Centi, G. (2006) Converting CO₂ to fuel: A Dream or a challenge? 232nd ACS National Meeting, San Francisco, CA, September.

Centrec (2009a) Economic Impacts of Biodiesel Production on the Soybean Sector, prepared for United Soybean Board by Centrec Consulting Group, LLC.

Centrec (2009b) Soybeans and Biodiesel: Key Price Relationships, prepared for United Soybean Board by Centrec Consulting Group, LLC.

Cetane Energy, LLC. (2010) <http://cetaneenergy.com/default.aspx>

Chinnasamy, S., Bhatnagar, A., Hunt, A., and das, K. C. (2010) Microalgae Cultivation in A Wastewater Dominated by Carpet Mill Effluents for or Biofuel Applications. *Bioresource Technology* vol. 101, 3097–3105.

Chiu, Y., B. Walseth, and S. Suh (2009) "Water Embodied in Bioethanol in the United States." *Environ. Sci. Technol.* 43: 2688–2692.

CIWM (2007) "California Waste Stream Profiles." database from California Integrated Waste Management Board, Sacramento, CA. <http://www.ciwmb.ca.gov/Profiles/>.

CIWM (1999) "California Waste Stream Profiles." database from California Integrated Waste Management Board, Sacramento, CA. <http://www.ciwmb.ca.gov/Profiles/>.

CleanTech Group (2007) Refinery supplier UOP Intros Green Diesel. <http://cleantech.com/news/1347/refinery-supplier-uop-intros-green-di>., June by Dana Childs.

CNEWS (2009) "Canadian company nixes Idaho for ethanol plant, picks Saskatchewan," May. <http://cnews.canoe.ca/CNEWS/Environment/2008/05/09/5518886.html>.

Cobalt Biofuels (2008) <http://www.cobaltbiofuels.com/science-and-technology/> (accessed November 25, 2009).

Coltrain, D. (2002) "Biodiesel: Is It Worth Considering?" 2002 Risk and Profit Conference. Holiday Inn, Manhattan, Kansas: August 15-16, 2002.

Committee on Toxicants (2002) "Committee on Toxicants and Pathogens in Biosolids Applied to Land." *Biosolids Applied to Land: Advancing Standards and Practice*, The National Academies Press, Washington, D.C. <http://epa.gov/waterscience/biosolids/nas/complete.pdf>.

Connor M. and Liao J. (2009) Microbial production of advanced transportation fuels in non-natural hosts. *CURRENT OPINION IN BIOTECHNOLOGY*:307-315.

ConocoPhillips (2006) News Release - ConocoPhillips begins production of renewable diesel fuel at Whitegate Refinery in Cork, Ireland.

Coskata (2010) <http://www.coskata.com/>

Coskata (2009) "Coskata Presentation." *Biofuels Development Summit, April 20-21*. Washington, D.C.: <http://www.ascension-publishing.com/BIZ/ABDSCoskata.pdf>.

Coughlin, K. and D. Fridley (2008) Physical Energy Accounting for California: A Case Study of Cellulosic Ethanol Production. California Energy Commission, PIER-Energy-Related Environmental Research Program. CEC-500-2009-007.

CRC Report: E-87-1 (2009) Mid-Level Ethanol Blends Catalyst Durability Study Screening.

Crutzen, P. J., A. R. Mosier, K. A. Smith, and W. Winiwarter (2008) "N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels." *Atmos. Chem. Phys.*, 8: 389 - 395.

Curtis, B. (2008) "U. S. Ethanol Industry, the Next Inflection Point."

Daggolu, P., S. Liu, and M. G. White (2007) Biomass Conversion over Acidic Solids and Supported Metals Catalysts.

http://www.propanecouncil.org/uploadedFiles/propanecouncil/About/Mission_Areas/Research_and_Development/Project_Summaries/12335_MSU_BioPropane_FinalReport.pdf: Dave C. Swalm School of Chemical Engineering; Mississippi State University Mississippi State, MS 39762.

Davis, R. D. (1996) "The Impact of EU and UK Environmental Pressures on the Future of Sludge Treatment and Disposal." *Water and Environment Journal*, Vol. 10, No. 1, February: 65-69.

De Baere, L. and Mattheeuws, B. (2010) 2010 Update and Trends – Anaerobic Digestion of MSW in Europe, Vol. 51, pp. 24-26.

Delucchi, M.A. (2006) Lifecycle Analyses of Biofuels, May, Report from the Institute of Transportation Studies, University of California, Davis, May.

Desa, E. (2001) "Submarine methane hydrates potential fuel resource of the 21st century", See http://drs.nio.org/drs/bitstream/2264/454/1/Proc_AP_Akad_Sci_5_101.pdf.

DOE (2010a) Dedicated Ethanol Pipeline Feasibility Study – Report to Congress. March, http://www1.eere.energy.gov/biomass/pdfs/report_to_congress_ethanol_pipeline.pdf

DOE (2010b).

http://www1.eere.energy.gov/hydrogenandfuelcells/production/photo_processes.html.

DOE (2010c).

http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/fc_comparison_chart.pdf
Comparison of Fuel Cell Technology.

DOE (2010d) California Team to Receive up to \$122 Million for Energy Innovation Hub to Develop Method to Produce Fuels from Sunlight

DOE (2010e) Methane Hydrate- The Gas Resource of the Future.

<http://fossil.energy.gov/programs/oilgas/hydrates/>.

DOE (2010f) <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/>

DOE (2009a) [Energy Innovation Hub Fuels from Sunlight](http://www.fedconnect.net/FedConnect/PublicPages/PublicSearch/Public_Opportunities.aspx), DE-FOA-0000214, http://www.fedconnect.net/FedConnect/PublicPages/PublicSearch/Public_Opportunities.aspx.

DOE (2009b) U.S. Department of Energy, Alternative Fuel Data Center, <http://www.afdc.energy.gov/afdc/data/fuels.html>.

DOE (2009c) U.S. Department of Energy - Energy Efficiency and Renewable Energy, Alternative Fuel Data Center, http://www.afdc.energy.gov/afdc/fuels/stations_counts.html, 2009.

DOE (2009d) U.S. Department of Energy - Energy Efficiency and Renewable Energy, Alternative Fuel Data Center, <http://www.afdc.energy.gov/afdc/data/vehicles.html>.

DOE (2009e) U.S. Department of Energy's Bioenergy Research Centers, An Overview of the Science, DOE/SC-01, July.

DOE (2009f) "National Algal Biofuels Technology Roadmap Draft Report of the December 9-10, 2008 Workshop." National Algal Biofuels Technology Workshop. U. S. Department of Energy Biomass Program.

DOE (2009g) Pathways to Commercial Success: Technologies and Products Supported by the Hydrogen, Fuel Cells & Infrastructure Technologies Program.

DOE (2009h) "Comparative Assessment of Advanced Gas Hydrate Production Methods", See http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_42666AssessProdMethods.html

DOE (2008a) Hydrogen Fuel Cells Fact Sheet.

DOE (2008b) "Methane Hydrate Program Report to Congress." http://fossil.energy.gov/programs/oilgas/publications/methane_hydrates/2008_Report_to_Congress-final.pdf.

DOE (2007a) Hydrogen, Fuel Cell & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan. <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html>

DOE (2007b) Validation of Hydrogen Fuel Cell Vehicle and Infrastructure Technology, <http://www.afdc.energy.gov/afdc/pdfs/42284.pdf>.

DOE (2007c) Multi-Year Research, Development and Demonstration Plan.

DOE (2007d) U.S. Department of Energy - Energy Efficiency and Renewable Energy, Alternative Fuel Data Center, http://www.afdc.energy.gov/afdc/fuels/hydrogen_distribution.html.

DOE (2007e) "Methane Hydrate: Future Energy within Our Grasp", See http://www.fossil.energy.gov/programs/oilgas/publications/methane_hydrates/MHydrate_overview_06-2007.pdf

DOE (2006a) Breaking the Biological Barriers to Cellulosic Ethanol: A Joint Research Agenda, A Research Roadmap Resulting from the Biomass to Biofuels Workshop. DOE/SC-0095, 2006.

DOE (2006b) “Hydrogen Production”,
http://www.hydrogen.energy.gov/pdfs/doe_h2_production.pdf.

DOE (2005a) http://www1.eere.energy.gov/hydrogenandfuelcells/news_cost_goal.html.

DOE (2003) Basic Research Needs for the Hydrogen Economy, Report of the Basic Energy Science Workshop on Hydrogen Production, Storage, and Use

DOE Report (2005b) Solar and Wind Technologies for Hydrogen Production, Report to Congress, ECECS EE-3060..

DOE website (2010c) Fuel Cell Accomplishments and Progress.
<http://www1.eere.energy.gov/hydrogenandfuelcells/accomplishments.html>

Dolan, G. (2008) Methanol Fuels: The Time has Come. presentation at the 17th ISAF conference, Taiyuan, China, October.

Duailibi, J. (2008) Ele é o falso vilão (in Portuguese). Veja Magazine. (2008-04-27).
http://www.pacificethanol.net/site/documents/news/PEIX.Forbearances_Extended_022609_FI_NAL.pdf.

Dupont, BP (2009), *Biobutanol Fact Sheet*.

Durbin, T.D., Karavalakis, G., Norbeck, J.M. (2010) Alternative Transportation Fuels Research Center, University of California at Riverside, under contract with CEC.

Durbin, T. D., Miller, J. W., Johnson, K., Hajbabaei, M. (2009) “Draft Final Memorandum, For the CE-CERT Engine Testing Portion for the CARB Assessment of the Emissions from the Use of Biodiesel as a Motor Vehicle Fuel in California ‘Biodiesel Characterization and NO_x Mitigation Study’”, Testing on 2006 Cummins ISM & 2007 MBE4000, Prepared for Mr. Bob Okamoto, CARB, October.

Durbin, T. D., and Miller, J. W. (2009b) Working Document on Literature Review for Evaluation of the Performance and Air Pollutant Emissions of Vehicles Operating on Various Natural Gas Blends. Prepared for Marla Mueller, California Energy Commission. College of Engineering, Center for Environmental Research and Technology, University of California, Riverside.

Durbin (2008) Comprehensive Assessment of the Emissions from the Use of Biodiesel in California – Regulated and Toxic Emissions. Coordinating Research Council Mobile Source Air Toxics Workshop, December, 2008.

Durbin, T. D., Welch, W. (2005). "Evaluation of Environmental Impacts of Thermochemical Conversion Technologies Using Municipal Solid Waste Feedstocks – Final Summary Report." University of California, Riverside.

Eberle, U. (2006) GM Research Strategy: Towards a Hydrogen-Based Transportation system. Funchy Workshop, Hamburg, Sept.

EIA (2010) Energy Information Agency, Updates for 2008, http://www.eia.doe.gov/emeu/states/_seds.html.

EIA (2009) Energy Information Agency, Monthly Energy Review, October 2009. www.eia.doe.gov/mer/DOE/EIA-0035 (2009/10).

EISA. (2007) Energy Independence and Security Act of 2007. http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=110_cong_bills&docid=f:h6enr.txt.pdf.

Enerkem (2010) <http://www.enerkem.com/index.php?module=CMS>.

Engineers Edge (2010) http://www.engineersedge.com/fluid_flow/fluid_data.htm

EPACT (1992) <http://www1.eere.energy.gov/femp/regulations/epact1992.html>.

EPM (2009) "Ethanol producers look to rebound from bankruptcy." Ethanol Producer Magazine, April. http://www.ethanolproducer.com/article.jsp?article_id=5450.

ExxonMobil (2010) ExxonMobil Algae Biofuels Research and Development Program brochure. http://www.exxonmobil.com/corporate/files/news_pub_algae_brochure.pdf.

Ezeji, T.C., Qureshi, N., Blascheck, H.P. (2004) Butanol Fermentation Research: Upstream and Downstream Manipulations, The Chemical Record, Vol. 4, 305–314.

FAA – Federal Aviation Administration (2009) Special Airworthiness Bulletin No. NE-09-25R1.

Falkowski, P. (2010) Developing Hypothesis-Driven Algal Biofuels Research. Algal Biofuels Symposium 2010, La Jolla. Not Published.

Fargione, J., Hill, D., Tilman, S., Polasky, and P. Hawthorne (2008) "Land Clearing and the Biofuel Carbon Debt." Science, Vol 319, 02 29, 2008: 1235 - 1238.

FAO – Food and Agriculture Organization of the United Nations (2010) Algae-Based biofuels - Applications and Products, Rome, Italy, July.

Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M. (2006) "Ethanol Can Contribute to Energy and Environmental Goals." Science 311, January (DOE/SC-0095), 07 2006: 506 - 508.

FreedomCar and Partnership (2009a) Hydrogen Production - Overview of Technology Options.
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/h2_tech_roadmap.pdf.

FreedomCar and Partnership (2009b) Hydrogen Production Roadmap, Technology Pathway to the Future.
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/h2_production_roadmap.pdf.

Fritsche, U. et al. (2008) The "iLUC Factor" as a Means to Hedge Risks of GHG Emissions from Indirect Land-Use Change Associated with Bioenergy Feedstock Provision. Cited by Gallagher: working paper prepared for BMU, Darmstadt (forthcoming), Oeko-Institut, 389 - 395.

Fulcrum Bioenergy (2010) See <http://fulcrum-bioenergy.com/>

GADA (2008) "Ethanol Tax Credit Reduced January 1 2009." Gasoline & Automotive Dealers of America., 12 31, 2008: <http://www.gasda.org/Lists/Announcements/DispForm.aspx?ID=33>.

Gallager, E. (2008) The Gallagher Review of the indirect effects of biofuels production. UK Renewable Fuels Association, July,
<http://www.gasda.org/Lists/Announcements/DispForm.aspx?ID=33>.

GAO (2009) Biofuels Potential Effects and Challenges of Required Increases in Production and Use Report to Congressional Requesters. GAO-09-446. United States Government Accountability Office, August.

Ghafoori, E., Flynn, P.C., and Feddes, J.J. (2007) Pipeline vs. truck transport of beef cattle manure. Biomass and Bioenergy. Vol 31. p. 168-175.

Goettemoeller, J., and A. Goettemoeller (2007) Sustainable Ethanol: Biofuels, Biorefineries, Cellulosic Biomass, Flex-Fuel Vehicles, and Sustainable Farming for Energy Independence. Praire Oak Publishing, Maryville, Missouri, p. 42. ISBN 9780978629304, 2007.

Gokhale, Z, R. Sayre, C. Stroff, and S. Pieris (2009) "Update of Algal research Activities." Presented at Biodiesel Technical Workshop, October, San Antonio, TX.

Goldemberg, J. (2008) "'The Brazilian biofuels industry.'" Biotechnology for Biofuels 2008, I:6. <http://www.biotechnologyforbiofuels.com/content/1/1/6>.

Golden, S. (2010) Cyanobacteria, the Other Algae. Algal Biofuels Symposium 2010,. La Jolla. Not published.

Goodenough, U. (2010) Lipid Body Formation Stimulated By Nitrogen Stress And Starch Knock Out in Chlamydomonas Reinhardtii. Algal Biofuels Symposium 2010,. La Jolla: Not published.

Graham, I.(2010) Air Force scientists test, develop bio jet fuels.
<http://www.af.mil/news/story.asp?id=123197415>.

Gray, D., White, C., Tomlinson, G., et al. (2007) Increasing Energy Security and Reducing Carbon Emissions of the U.S. Transportation Sector: A Transformational Role for Coal with Biomass. Report DOE/NETL – 2007/1298 prepared for the National Energy Technology Laboratory, Golden, CO.

Green chemicals (2009) Valero to Produce fat-based Green diesel. by Doris de Guzman, September.

Gronowska, M, S Joshi, and H. L. MacLean (2009) "A Review of U.S. and Candian Biomass Supply Studies." *Bioresources* 4(1): 341-369.

Grossman, A. (2010) Light and the production of biodiesel by algae; pros and cons.. *Algal Biofuels Symposium 2010, La Jolla*. Not published.

Hackett, C., Durbin, T. D., Welch, W, Pence, J/, Williams, R. B., Jenkins, B. M., Salour, D., Aldas, R. (2004) Draft Final Report: Evaluation of Conversion Technology Processes and Products, Prepared for Integrated Waste Management Board.

Hammerlinck, M. (2010) Minnesota Organizations to Jointly Fund Five Corn, Ethanol Research Projects. Press Release. May, 19.

Hannon, M, Gimpel, J., Tran, M., Beth Rasala, B., and Mayfield, S. (2010) Biofuels from algae: challenges and potential. In press.

Hansen, J.B., and S. Mikkelsen (2001) "DME as a Transportation Fuel."

Haque, M., F. M. Epplin, S. Aravindhakshan, and C. Taliaferro. (2008) "Cost to Produce Cellulosic Biomass Feedstock: Four Perennial Grass Species Compared." Southern Agricultural Economics Association Annual Meeting. Dallas, TX February.

Haskew, H. M., Liberty, T. F., and McClement, D. (2004) Fuel Permeation From Automotive Systems, CRC Project No. E-65.

Haskew, H. M., Liberty, T. F., and McClement, D. (2006) Fuel Permeation From Automotive Systems: E0, E6, E10, E20 and E85, CRC Project No. E-65-3.

Haskew & Associates (2001) "Literature Search Summary Emission Effects (Permeation) of Ethanol in Gasoline" <http://www.arb.ca.gov/fuels/gasoline/meeting/2001/LSSM0508.pdf>.

Heim, M., M. Martindale, and I. Wang (2007) "population Projections by Race/Ethnicity, Gender and Age for California and Its Counties 2000-2050." daabase from the State of California-department of Fincance, Sacramento, CA, July.
<http://www.dof.ca.gov/HTML/DEMOGRAP/ReportsPapers/Projections/P3/P3.php>.

Hertel, T.W., Golub, A.A., Jones, A.D., O'Hare, M., Plevin, R.J., and Kammen, D.M. (2010) Effects of US Maize Ethanol on Global Land Use and Greenhouse Gas Emissions: Estimating Market-mediated Responses. *Bioscience*, Vol. 60, p. 223.

Hill, J. E. Nelson, D. Tilman, S. Polasky, and , D. Tiffany (2006) "Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels." *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 103, No. 30, pp. 11206 – 11210, July 25.

Hisao Hori, H., and K. Koike (2005) "New Application of Glycerin from a Photochemical Approach: Dihydrogen Formation from Aqueous Glycerin by Use of Giant Polyoxometalate Photocatalysts." *Energy & Fuels* , 19: 2209-2213.

Hoekman, S. K., A. Gertler, A. Broch, and C. Robbins (2009) Investigation of Biodistillates as Potential Blendstocks for Transportation Fuels. CRC Project No. AVFL-17 Final Report, June, <http://www.gasda.org/Lists/Announcements/DispForm.aspx?ID=33>.

Holmgren, J., R. Marinangeli, P., P. Nair, D. Elliott, and R. Bain (2008) "Consider upgrading pyrolysis oils into renewable fuels,." *Hydrocarbon Processing*, September, 12, pp 95 - 103.

Howes, P., Bates, J., Jamieson, C., O'Brien, S., Webb, J., Barker, N., Sajwaj, T., Pridmore, A., Wiggins, S., Leturque, H., and Dale, N. (2009) Biofuels Research Gap Analysis. Final Report to the Biofuels Research Steering Group. ED45917, Issue Number 3, July 30, 2009. <http://www.dft.gov.uk/pgr/roads/environment/research/biofuelsresearch/researchdocument.pdf>.

Huang, H.J., Ramaswamy, S., Al-Dajani, W., et al. (2009) Effect of biomass species and plant size on cellulosic ethanol: A comparative process and economic analysis. *Biomass and Bioenergy*. Vol. 33. p. 234- 246.

Huber, G.W., O'Conner, P., Corma, A. (2007) Processing Biomass in Conventional Oil Refineries: Production of High Quality Diesel by Hydrotreating Vegetable Oils in Heavy Vacuum Oil Mixtures. *Applied Catalysis A: General*, vol. 329, pp. 120-129.

Humbird, D. and Aden, A. (2009) Biochemical Production of Ethanol from Corn Stover: 2008 State of Technology Model. National Renewable Energy Laboratory Technical Report No. NREL/TP-510-46214.

Hussain, S.T., and H. Rahman (2009) "Nano Catalyst for CO₂ Conversion to Hydrocarbons." *Journal of Nano Systems & Technology*, Vol. 1, No.1, Oct 31, 2009, JNST.2009.004: 1-9.

IFP (2010) Alternative Fuels for Transport, IFP-Brochure-Alternative-Fuels-VA-1.pdf, see <http://www.ifpenergiesnouvelles.com/antidot/search?context=default&keywords=exothermal+properties+&x=8&y=5>

Iki, H., Iguchi, Y., and Koyama, A. (2006) Applicability of Hydrogenated Palm Oil for Automotive Fuels. 16th Saudi Arabia-Japan Symposium, Dhahran, Saudi Arabia, November.

INEOS (2010) http://www.ineos.com/new_item.php?id_press=257.

INEOS (2009) INEOS Bio JV Selected for \$50 Million U.S. Department of Energy Grant for Commercial BioEnergy Facility. December 4. http://www.ineosbio.com/76-Press_releases-6.htm.

INEOS (2008) Cars to run on fuel from household waste within two years. July. http://www.ineosbio.com/76-Press_releases-2.htm.

International Biochar Initiative (2010) White Paper on Biochar: A Soil Amendment that Combats Global Warming and Improves Agricultural Sustainability and Environmental Impacts. www.biochar-international.org/images/White_Paper.doc.

Iogen (2010) <http://www.iogen.ca/>.

Iogen (2009) "*Shell first to sell gasoline blended with advanced biofuel*" October. http://www.iogen.ca/news_events/press_releases/2009_06_10_IogenOttawaDemoRelease_Canada.pdf.

Iwuchukwu, I. J., Vaughn, M., Myers, N., O'Neill, H., Frymier, P., and Bruce, B. D. (2009) Self-Organized Photosynthetic Nanoparticle For Cell-Free Hydrogen Production. *Nature Nanotechnology*, November 8, 2009: 1 - 7.

Jackson, N. (2006) Low Carbon Vehicle Strategies – Options and Potential Benefits. Cost Effective Low Carbon Engines Conference. I. Mech.E., London, November.

Jacobs, J. (2009) Ethanol from Sugar. <http://www.rurdev.usda.gov/rbs/pub/sep06/ethanol.htm>.

Jalonick, M. C. (2008) "Congress enacts \$290B farm bill over Bush veto." *The Seattle Times*, 05 22.

Jermisirisakpong, K., Vo, C., Park, C.S., Norbeck, J.M. (2010) Assessment of Uncertainties in Life Cycle and Energy Analyses of Production of Synthetic Fuels from Carbonaceous Feedstocks. Final Report Prepared by UCR CE-CERT for Honda R&D Co., Tochigi R&D Center, Tochigi, 321-3393 Japan.

Jobe, J. (2009) "State of the US Biodiesel Industry." Presented at 2009 Biodiesel Technical Workshop, October, San Antonio, TX.

Johannesson, C. (2008) "Wastewater Operations Manager at the Riverside Regional Water Quality Treatment Plant," personal correspondence.

Johnson, D. T, and K. A. Taconi. (2007) "The Glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production." *Environmental Progress*, Vol 26, Issue 4: 338-348.

Jones, A., M. O'hare, and A. Farrell (2007) Biofuel boundaries: Estimating the medium-term supply potential of domestic biofuels. Paper UCB-ITS-TSRC-RR-2007-4, University of California, Berkeley.

Jones, B., Mead, G., and Steveens, P. (2008a) The Effects of E20 on Plastic Automotive Fuel System Components.

<http://www.mda.state.mn.us/news/publications/renewable/ethanol/e20onplastics.pdf>

Jones, B., Mead, G., Steevens, P., and Timanus, M. (2008b) The Effects of E20 on Metals Used in Automotive Fuel System Components.

<http://www.mda.state.mn.us/news/publications/renewable/ethanol/e20onmetals.pdf>

Jones, B., Mead, G., Steevens, P., and Connors, C. (2008c) The Effects of E20 on Elastomers Used in Automotive Fuel System Components.

<http://www.mda.state.mn.us/news/publications/renewable/ethanol/e20onelastomers.pdf>

Kadam, K. L., et al. (1999) "Environmental life Cycle Implications of Fuel Oxygenate Production from California Biomass." report NREL/TP-580-25688 prepared for National Renewable Energy Laboratories, Golden, CO, May,

<http://www.nrel.gov/docs/fy99osti/25688.pdf>.

Kanan, M. W., and Nocera, D. G. (2008) In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+} . Science 22 August 2008: Vol. 321. no. 5892, 2008: 1072 - 1075.

Kang, S., J. K. Bae, H. Kim, G. M. Dhar, and K. Jun (2010) Enhanced Catalytic Performance for Dimethyl Ether Synthesis from Syngas with the Addition of Zr or Ga on a Biofunctional Catalyst." Energy & Fuels, 24: 804-510.

Kinder Morgan (2009) "Kinder Morgan Florida Pipeline Ethanol Project."

http://www.afdc.energy.gov/afdc/pdfs/km_cfpl_ethanol_pipeline_fact_sheet.pdf

Kittelson, D., Tan, A., and Zarling, D. (2008) Demonstration and Driveability Project to Determine the Feasibility of Using E20 as a Motor Fuel. Final report submitted to Minnesota Department of Agriculture.

<http://www.mda.state.mn.us/news/publications/renewable/ethanol/e20drivability.pdf>

Kittrell, J. R. (2007) Final Report: Technology for Enhanced Biodiesel Economics, EPA Contract Number: EPD07052,

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/8333/report/F

Kittrell, J. R. (2008) Technology for Enhanced Biodiesel Economics, EPA Contract Number: EPD08061 from May 1, 2008 through April 30, 2010,

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.highlight/abstract/8753.

Kleinschek, G. (2005) Emission Tests with Synthetic Diesel Fuels (GTL & BTL) with a Modern Euor 4 (EGR) Engine. Kolloquium "Fuels" der Technischen Akademie Esslingen (TAE), January.

Knoll, K., West, B., Clark, W., Graves, R., Orban, J., Przesmitzki, S., and Theiss, T. (2009) Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1 – Updated.

Korves, R. (2008) The Potential Role for Corn Ethanol in Meeting the Energy Needs of the United States in 2016-2030. Report for the Illinois Corn Marketing Board, October.

Krahl, J, et al. (2009) Comparison of exhaust emissions and their mutagenicity from the combustion of biodiesel, vegetable oil, gas-to-liquid and petrodiesel fuels. Fuel no.88, pp. 1064–1069.

Krich, K., D. Augenstein, J. P. Batmale, J. Benemann, B. Rutledge, and D. Salour (2005) Biomethane from Dairy Waste, A Sourcebook for the Production and Use of Renewable Natural Gas in California. July. http://www.suscon.org/cowpower/biomethaneSourcebook/Full_Rep.

Kromer, and Heywood (2007) "Electric Powertrains: Opportunities & Challenges in the U.S. Light-Duty Vehicle Fleet Report # LFEE 2007-03RP. MIT, May.

Kruse, J., Ramsey, S., and Jackson, T. (2008) Life Cycle Analysis of Greenhouse Gas Emissions Associated with Starch-Based Ethanol. prepared by Global Insight for The American Coalition for Ethanol, December.

Kumarappan, S., S. Joshi, and H. L. MacLean. (2009) "Biomass Supply for Biofuel Production: Estimates for the United States and Canada." BioResources 4(3): 1070 - 1087.

Kuronen, M., Mikkonen, S., Aakko, P., Murtonen, T. (2007) Hydrotreated Vegetable Oil as Fuel for Heavy-Duty Diesel Engines. SAE Technical Paper No. 2007-01-4031.

Lane, J., (2010), "Jet Stream; Biofuels Digest Special report on Aviation Biofuels", Biofuels Digest, March 3, <http://biofuelsdigest.com/bdigest/2010/03/03/jet-stream-biofuels-digest-special-report-on-aviation-biofuels/>

Lappas, A.A., Bezergianni, S., Vasalos, I.A. (2009) Production of Biofuels via Co-processing in Conventional Refining Processes, Catalysis Today, Vol. 145, pp. 55-62.

Lazarus, W. (2008) Energy Crop Production Costs and Breakeven Prices under Minnesota Conditions. Department of Applied Economics, University of Minnesota: Staff Paper Series, Staff Paper P08-11.

Lehmann, J., da Silva, J.P., Steiner, C., Nehls, T., Zech, W., and Glaser, B. (2003) Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments, Plant & Soil, vol. 249, pp. 343-357.

Liss, W.E. (2006) Light-duty CNG Vehicle Fuel Composition Study. Topical Report, GTI Project No. 20245, April.

Liu, C., B. Xue, B. Eliasson, F. He, Y. Li, and G. Xu (2001) "Methane Conversion to Higher Hydrocarbons in the Presence of Carbon Dioxide Using Dielectric-Barrier Discharge Plasmas." *Plasma Chemistry and Plasma Processing*, Vol. 21, No. 3: 301-310.

LS9 Website (2010) <http://www.ls9.com/technology/>.

Lynd, L.R., Laser, M.S., Bransby, D., Dale, B.E., Davison, B., Hamilton, R., Himmel, M., Keller, M., McMillan, J.D., Sheehan, J., and Wyman, C.E. (2008) How biotech can transform biofuels. *Nature Biotech.*, Vol. 26, p. 169.

Lynn, J. (2009) Can Methanol Really Make a Dent in US Oil Demand? *Energy Tribune*, July 29. <http://www.energytribune.com/articles.cfm?aid=2131>

MacDonald, T. (2005) Alcohol Fuel Flexibility - Progress and Projects. 15th International Symposium on Alcohol Fuels, San Diego, September, California Energy Commission Report # CEC-600-2005-038.

Macedo, I., M. L. Verde Leal, and J. A. R. da Silva (2004) Assessment of greenhouse gas emissions in the production and use of fuel ethanol in Brazil 2004. <http://www.wilsoncenter.org/events/docs/brazil.unicamp.macedo.greenhousegas.pdf>.

Malcolm, S. and Aillery, M. (2009) "Growing Crops for Biofuels Has Spillover Effects", *Amber Waves*, March, <http://www.ers.usda.gov/amberwaves/march09/features/biofuels.htm>

Mankato, (2009) "E20: The Feasibility of 20 Percent Ethanol Blends by Volume as a Motor Fuel", Executive Summary, Results of Materials Compatibility and Drivability Testing. http://www.growthenergy.org/images/reports/minnesota_e20execsumm.pdf

Martini, G. (2007) Joint EUCAR/JRC/CONCAWE Study on: Effects of Gasoline Vapour Pressure and Ethanol Content on Evaporative Emissions from Modern Cars.

Mascoma (2010) See <http://www.mascoma.com/pages/index.php>.

McCormick, R.L.; Alleman, T.L.; Ratcliff, M.; Moens, L.; Lawrence, R. (2005) *Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004*; NREL/TP-540-38836; National Renewable Energy Laboratory: Golden, CO, October; <http://www.nrel.gov/docs/fy06osti/38836.pdf>.

McCormick, R.L., Williams, A., Ireland, J., Brimhall, M., and Hayes, R.R., (2006) Effects of Biodiesel Blends on Vehicle Emissions. Technical report for NREL, report No. NREL/MP-540-40554.

McElroy, A.K. (2007) Pipeline Potential. *Biodiesel Magazine*, February.

McKeever, D. B. (2004) "Inventories of Woody Residues and Solid Wood Waste in the United States, 2002." Ninth International Conference on Inorganic-Bonded Composite Materials, Vancouver, British Columbia, October.

http://www.fpl.fs.fed.us/documnts/pdf2004/fpl_2004_mckeever002.pdf.

Mead, G., Jones, B., Steevens, P., Hanson N., and Harrenstein, J. (2009) An Examination of Fuel Pumps and Sending Units During a 4000 Hour Endurance Test in E20.

Milbrandt, A. (2005) A Geographic Perspective on the Current Biomass Resource Availability in the United States. National Renewable Energy Laboratory Technical Report, NREL/TP-560-39181, December.

http://seattletimes.nwsourc.com/html/politics/2004431073_apcongressfarmbill.html.

Mintz, M., Folga, S., Molburg, J., Gillette, J. (2002) Cost of Some Hydrogen Fuel Infrastructure Options, Argonne National Laboratory, Transportatio Technology R&D Center, January 16, 2002.

Moller, R. M. (2005) Brief on Biomass and Cellulosic Ethanol report CRB 05-010 prepared for California Research Bureau, Sacramento, CA December.

<http://www.libraryh.ca.gov/crb/05/10/05-010.pdf>.

Morello, J. and Pate, R. (2010) The Promise and Challenge of Algae as Renewable Sources of Biofuels, US DOE Biomass Program Webinar, September 8.

Mosier, Warner (2007) "Ethanol from Cellulose Resources," University of Tennessee, SunGrant Initiative.

Mouawad, J. (2008) "Pumping Hydrogen." NY Times, September 23.

NAABB Website (2010) <http://www.naabb.org/>

Nam, S., H. Kim, G. Kishan, M. Choi, and K. Lee. (1999) "Catalytic conversion of carbon dioxide into hydrocarbons over iron supported on alkali ion-exchanged Y-zeolite catalysts." Applied Catalysis A: General 179: 155-163.

National Research Council (2004) The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs. Washington, DC: National Academy Press.

National Science Foundation (2009) Efficient Photocatalytic Conversion of CO₂ and Water Vapor to Hydrocarbon Fuels Using Sunlight.

http://nsf.gov/awardsearch/showAward.do?AwardNumber=0927262&WT.z_pims_id=13360.

NASA News (2009) <http://www.nasa.gov/centers/ames/news/releases/2009/09-147AR.html>.

Navigant, Consulting (2008) "North American Natural Gas Supply Assessment" Prepared for American Clean Skies Foundation. Chicago, Illinois: Navigant Consulting, July 4, 2008, Vol. 2, pp 148–173.

NBB - National Biodiesel Board (2009a) U. S. Biodiesel Production Capacity. June 22, 2009. See http://www.biodiesel.org/pdf_files/fuelsheets/Production_Capacity.pdf

NBB - National Biodiesel Board. (2009b) http://www.biodiesel.org/pdf_files/fuelsheets/Production_Graph_Slide.pdf.

NBB - National Biodiesel Board (2009c) The Biodiesel Bulletin. July.

NBB - National Biodiesel Board (2009) news release, <http://nbb.grassroots.com/09Releases/BioheatFuture/>.

Nejame, S. (2010) Butanol as A Fuel – View From The Field, Presentation at NREL, March.

Neste Oil (2010) <http://www.nesteoil.com>.

NETL (2009) "Methane Hydrates R&D Program: Today and Tomorrow", http://www.fossil.energy.gov/programs/oilgas/publications/Factsheets/NETL_MHydrateProg_2009.pdf

NETL (2007) "Interagency Coordination on Methane Hydrates R&D", <http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/pdf/InteragencyPrint.pdf>

Nichols, R.J. (2003) The Methanol Story: A Sustainable Fuel for the Future. Journal of Scientific & Industrial Research. Vol. 62, pp. 97-105. http://www.tracked.com/company/nippon_oil/news/.

Nimblett, J. and Ruppel, C. (2003) Permeability evolution during the formation of gas hydrates in marine sediments. J. Geophysical Research, vol. 108, No. B9, 2420.

Norbeck, J. M., C. S. Park, A. S. K. Raju, and C. Vo (2008) "Suitability of the Steam Hydrogasification Process to Convert Biomass Materials Prevalent in Southern California into Synthetic Transportation Fuels." Final Report to the California Energy Commission from the University of California at Riverside under Contract No. 500-99-013, September.

Norbeck, J.M., J.W. Heffel, T.D. Durbin, B. Tabbara, J.M. Bowden, and M.C. Montano (1996) "Hydrogen Fuel for Surface Transportation." Published by the Society of Automotive Engineers, Warrendale, PA.

Norman, K. (2007) Interim Report, Feasibility of Microscale Glucose Reforming for Renewable Hydrogen. Albuquerque, NM: Sandia National Laboratories, SAND2007-1713.

North Carolina Department of Environment and Natural Resources (1999) A Fact Sheet for Restaurant Oil and Grease Rendering. October. <http://www.p2pays.org/ref/03/02791.pdf>.

NRC (2008) Review of the Research Program of the Freedom CAR and Fuel Partnership: Second Report. March. National Research Council.

NRDC – National Resources Defense Council (2009) Cultivating Clean Energy: The Promise of Algae Biofuels. www.nrdc.org/energy/files/fcultivating.pdf.

NREL (2007) Hydrogen Technologies.

<http://www.afdc.energy.gov/afdc/pdfs/42284.pdf>. (accessed February 25, 2010).

NREL (2009) Biodiesel Handling and Use Guide, Fourth Edition. NREL/TP-540-43672.

Nuernberg, T. (2009) "'Breaking through the Blend Wall'." Ethanol Producer Magazine. January. http://www.ethanolproducer.com/article.jsp?article_id=5151.

Nunez. (2007) "Alternative fuels and vehicle technologies: funding programs." Assembly Bill 118, Chapter 750. , California statutes of 2007.

Nunez/Pavley (2006) "The California global warming solutions act, California statutes of 2006." Assembly Bill 32 Chapter 488. California Assembly.

Ohno, Y. (2007) New Clean Fuel DME, DeWitt Global Methanol & MTBE Conference (Bangkok, March 12-14 2007).

Orbital Engine Company (2004) "Market Barriers to the Uptake of Biofuels Study Testing Gasoline Containing 20% Ethanol (E20)," Phase 2B Final Report to the Department of the Environment and Heritage, May.

Osava, M. (2008) Brazil on verge of clean petroleum product. March 23.

<http://www.speroforum.com/site/article.asp?idarticle=14837>.

Oxfam (2008) Another Inconvenient Truth. 06 28, 2008.

http://www.oxfam.org.uk/resources/policy/climate_change/downloads/bp114_inconvenient_truth.pdf.

Pacific Ethanol (2010) Pacific Ethanol, Inc. Plans to Restart Stockton, California Ethanol Production Facility within 60 Days, press release, October. <http://www.pacificethanol.net/>

Patzek, T., (2004) Crit. Rev. Plant Sci., vol. 23, p. 519.

Pavley (2005) "Air quality: alternative fuels." Assembly Bill No. 1007, CHAPTER 371. California Assembly.

Pearson, R.J., Turner, J.W.G., Eisaman, M.D., and Littau, K.A. (2009) Extending the Supply of Alcohol Fuels for Energy Security and Carbon Reduction, SAE 2009-01-2764.

Peralta-Yahya, P.P. and Keasling, J.D. (2010) Advanced biofuel production in microbes. *Biotechnol. J.*, vol. 5, 147–162.

PERC (2010) Propane Education and Research Council,

<http://www.propanecouncil.org/Fleet.aspx?id=3316>.

Perlack, R. D., L. L. Wright, A. F. Turhollow, R. L. Graham, B. Stokes, and J. Erbach (2005) Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply. DOE Contract DE-AC05-000R22725, DOE/GO-102005-2135, ORNL/TM-2005/66, April,

http://seattletimes.nwsourc.com/html/politics/2004431073_apcongressfarmbill.html.

Perrone, M. (2008) "Ethanol is Not to Blame for Higher Food Prices." May 1. <http://autos.aol.com/article/ethanol-higher-food-prices>.

Persson, M, Jonsson, O. and Wellinger, A. (2006) Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. IEA Bioenergy, Task 37. Energy from Biogas and Landfill Gas, December 2006. http://www.iea-biogas.net/Dokumente/upgrading_report_final.pdf.

Petrobras (2010) <http://www2.petrobras.com.br/tecnologia/ing/hbio.asp>.

Phillips, S., A. Aden, J. Jechura, D. Dayton, and T. Eggeman (2007) Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. NREL/TP-510-41168.

Phycal (2009) http://www.phycal.com/closer_look.html.

Pimentel, D. and Patzek, T. (2005) Nat. Resour. Res., vol. 14, p. 65.

Plevin, R, A. Jones, and M. O'Hare. (2008) "Uncertainty analysis of land-use change carbon releases." EEA Expert Meeting, Copenhagen.

POET (2010) See <http://www.poet.com/>.

POET. (2009) "*On first anniversary of pilot plant start-up, POET announces cost reductions in cellulosic ethanol*". November. <http://www.poetenergy.com/news/showRelease.asp?id=181>.

Poon Y. (2010) Algal engineering for the production of an energy crop [Conference]// Algal Biofuels Symposium 2010.- La Jolla, CA: Unpublished, 2010.- Vols. Held April 23.

Pore, R. (2010) EPA approves limited use of E15 in U.S. vehicle fleet. Aglines, October. <http://www.aglines.com/2010/10/epa-approves-limited-use-of-e15-in-u-s-vehicle-fleet/>

Prince, R. C., and Kheshgi, H. S. (2005) The Photobiological Production of Hydrogen: Potential Efficiency and Effectiveness as a Renewable Fuel. Critical Reviews in Microbiology, 2005: 31: 1, 19 — 31.

Qureshi, N. and Ezeji, T. C. (2008) Butanol, 'a superior biofuel' production from agricultural residues (renewable biomass): recent progress in technology, Biofuels, Bioprod. Bioref. 2:319–330.

Rajagopal, D. and D. Zilberman (2007) Review of Environmental, Economic and Policy Aspects of Biofuels. Policy Research Working Paper 4341, The World Bank, Development Research Group, Sustainable Rural and Urban Development Team.

Ramey, D, and Shang-Tian Yang (2004) Production of Butyric Acid and Butanol from Biomass. Final Report under Contract No: DE-F-GO2-00ER86106 for U.S. Department of Energy, Morgantown, WV.

Randolph, N. (2009) State Grant Powers Up Menon's Biowaste-to-Biofuels Technology. San Diego Business Journal, October, <http://www.allbusiness.com/government/government-bodies-offices/13301762-1.html>.

Range Fuels (2010) <http://www.rangefuels.com/>

Range Fuels (2009) "U.S. Department of Agriculture Awards Range Fuels an \$80 Million Loan Guarantee". January 19. <http://www.rangefuels.com/u.s.-department-of-agriculture-awards-range-fuels.html>.

Rapport, J., Zhang, R., Jenkins, B.M., and Williams, R.B. (2008) Current Anaerobic Digestion Technologies Used for Treatment of Municipal Organic Solid Waste. California Integrated Waste Management Report No. IWMB-2008-011, March.

Reuter, R.M., Hochhauser, A.M., Benson, J.D., Koehl, W.J., Burns, V.R., Painter, L.J., Gorse, Jr., R.A., Rippon, B.H., Rutherford, J.A. (1992) "Effects of Oxygenated Fuels on RVP on Automotive Emissions – Auto/Oil Air Quality Improvement Program," SAE Technical Paper No. 920326, SAE, Warrendale, PA.

RFA (2010) "Climate of Opportunity." 2010 Industry Outlook, <http://www.ethanolrfa.org/pages/annual-industry-outlook>.

RFA (2009) "Climate of Opportunity." 2009 Industry Outlook, http://www.ethanolrfa.org/page/-/objects/pdf/outlook/RFA_Outlook_2009.pdf?nocdn=1

Riduan, S. N., Zhang, y., and Ying, J. (2009) Conversion of Carbon Dioxide into Methanol with Silanes over N-Heterocyclic Carbene Catalysts, *Angew. Chem. Int. Ed.* 2009, 48, 3322 –3325.

Ringer, M., V. Ptusche, and J. and Scahill (2006) Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis. Technical Report NREL/TP-510-37779.

RFS1 (2007) 40 CFR Part 80 Regulation of Fuels and Fuel Additives: Renewable Fuel Standard Program; Final Rule, May 1.

RFS2 (2010) 40 CFR Part 80 Regulation of Fuels and Fuel Additives: Changes to Renewable Fuel Standard Program; Final Rule, March 26.

RISE (2010) <http://www.rise.org.au/info/res/biomass/index.html>.

Rodgers, D. (2009) The US Biomass Energy Program –Transition to the Development and Implementation of Fungible Fuel Technologies. Department of Energy Presentation.

Ross A.B., Jones J.M., Kubacki M.L. and Bridgeman T. (2008a) Classification of macroalgae as fuel and its thermochemical behavior. *Bioresource Technology* Vol. 99, pp 6494–6504.

Ross A.B., Anastasakisa K., Kubackia M. and Jonesa J.M. (2008b) Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA. *J. of Anal. and App. Pyrolysis* Vol. 85, Iss. 1-2, May, pp 3-10.

Rothe, D., Lorenz, J., Lammermann, R., Jacobi, E., Rantanen, L., Linnaila, R. (2005) New BTL Diesel Reduces Effectively Emissions of a Modern Heavy-Duty Engine. Kolloquium “Fuels” der Technischen Akademie Esslingen (TAE), January.

Rother, L. (2006) "With Big Boost From Sugar Cane, Brazil Is Satisfying Its Fuel Needs." *The New York Times*, 04 10, 2006,
<http://www.nytimes.com/2006/04/10/world/americas/10brazil.html?pagewanted=1&sq=Bush%20Brazil%20ethanol&st=nyt&scp=5>.

Sanford, S. D., White, J. M., Shah, P. S., Wee, C. M., Valverde, J., and Meier, G. R. (2009) Feedstock and Biodiesel Characteristics Report. Renewable Energy Group, Inc., www.regfuel.com.

Sapphire Energy (2010) www.sapphireenergy.com.

Schwarzenegger, A. (2007) "Executive Order S-01-07." Sacramento, California, January 18.

Schwarzenegger, A. (2006) "Executive Order S-06-06." Sacramento, California, April 25.

Searchinger, T, et al. (2008) "Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change." *Science* 319: doi:10.1126/science. (IEA Bioenergy, Task 37 – Energy from Biogas and Landfill Gas, December 2006), 5: 1238 - 1240.

Searcy, E. & Flynn, P.C. (2010) To be submitted. A criterion for selecting renewable energy processes. Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada.

Semelsberger, T. A., R., L. Borup, and L. Greene H. (2006) "Dimethyl ether (DME) as an alternative fuel." *Journal of Power Sources* 156: 497–511.

Shanghai Daily (2008) DEM to Brighten China's Energy Future.
http://times.busytrade.com/1546/1/DEM_to_Brighten_China_s_Energy_Future.html

Shapouri, H. and Salassi, M., (2006), The Economic feasibility of Ethanol Production from Sugar in the United States, see <http://www.usda.gov/oce/reports/energy/EthanolSugarFeasibilityReport3.pdf>

Sheehan J., Dunahay T.G., Benemann J.R., Roessler P.G., Weissman J.C. (1998) A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae National Renewable Energy Laboratory Report NREL/TP-580-24190.

Solazyme (2010) www.solazyme.com.

Steen E. (2010) Microbial production of fatty-acid-derived fuels and chemicals from plant biomass, *Nature* **463**, 559-562, 2010.

STO (2010a) Biofuels. <http://www.darpa.mil/sto/chembio/biofuels.html>.

STO (2010b) Biofuels Alternative.
http://www.darpa.mil/sto/chembio/biofuels_alternative.html

Synthetic Genomics, Inc. (2010) www.syntheticgenomics.com.

Tachinardi, M. H. (2008) "Por que a cana é melhor que o milho (in Portuguese)." *Época Magazine*.*Época Magazine*. (2008-06-13). Print edition pp. 73, 06 13, 2008: *Época Magazine*. (2008-06-13). <http://revistaepoca.globo.com/Revista/Epoca/0,,EMI5865-15273.html>.

Tao, L. and Aden, A., (2009) The Economics of Current and Future Biofuels, *In Vitro Cell. Dev. Biol. – Plant*, vol. 45 pp. 199-217.

TCPalm.com (2009) "*Vero Beach firm may get federal grant for alternate energy plant near Indian River landfill*". December 4. <http://www.tcpalm.com/news/2009/dec/04/vero-beach-company-may-get-federal-grant-for/>.

The National Academies (2004) March 3.
http://www7.nationalacademies.org/ocga/testimony/Reviewing_Hydrogen_Fuel_FreedomCAR_Initiatives.asp (accessed November 25, 2009).

Tonkovich A. L. (2009) Improved Fischer-Tropsch Economics Enabled by Microchannel Technology. http://www.velocys.com/docs/Microchannel_FT_White_Paper_Sep08.pdf.

Transportation Research Center, Inc. (2009) CRC Report: E-87-1: Mid-Level Ethanol Blends Catalyst Durability Study Screening, Final Report to the Coordinating Research Council, July.

United Nations (2009) FAOSTAT, Food and Agriculture Organization of the United Nations, <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor>

Univenture, Inc and AlgaeVenture Systems, LLC, 2009 Harvesting, Dewatering, and Drying Technology. March 15. <http://www.algaevs.com/products-technology> (accessed December 8).

University of California, Riverside (2009) Evaluation of Emissions from Thermal Conversion Technologies Processing Municipal Solid Waste and Biomass, Final report for the BioEnergy Producers Association.

University of Sheffield (2008). Fuel From Bacteria Is One Step Closer. *ScienceDaily*. Retrieved November 10, 2010, from <http://www.sciencedaily.com/releases/2008/08/080806113141.htm>, August 8.

Urquhart, J. (2009) "Easier ester synthesis." *Chemistry World*, December: <http://www.rsc.org/chemistryworld/News/2009/December/04120901.asp>.

USB (2009) Food & Fuel, Meeting the Challenges of Feeding the World and Creating Renewable Fuel, presented by United Soybean Board.

U. S. Congress (2005) "Energy Policy Act of 2005." 42 USC 15801, Public Law 109-58, 109th Congress, August 8.

US EPA (2010) Partial Grant and Partial Denial of Clean Air Act Waiver Application Submitted by Growth Energy to Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator, October, Docket ID No. EPA-HQOAR-2009-0211. <http://www.epa.gov/otaq/regs/fuels/additive/e15/e15-waiver-decision.pdf>.

US EPA (2002) Draft Technical Report, *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions*, EPA420-P-02-001, October.

US EPA CHP Partnership (2007) "Impact of CHP on Energy and Carbon Emissions in the Dry Mill Ethanol Process."

USEIA (2010a) U. S. Energy Information Administration, Independent Statistics and Analysis, Natural Gas, See http://www.eia.doe.gov/dnav/ng/ng_prod_top.asp

USEIA (2010) "Estimated Number of Liquefied Petroleum Gas (LPG) Vehicles in Use by User Group and State." http://www.eia.doe.gov/cneaf/alternate/page/atftables/attf_v14.html.

USFCC (2009) U.S. Fuel Cell Council Commercially Available Fuel Cell and Fuel Cell-Related Products List.

USGS (2008) "Assessment of Gas Hydrate Resources On The North Slope, Alaska", http://pubs.usgs.gov/fs/2008/3073/pdf/FS08-3073_508.pdf.

Varghese, O. K., M. Paulose, T.J. LaTempa, and C. A. Grimes (2009) "High-Rate Solar Photocatalytic Conversion of CO₂ and Water Vapor to Hydrocarbon Fuels." *NANO LETTERS*, Vol. 9, No. 2: 731-737.

Voegele, E. (2009) "Sugarcane Economics". *Ethanol Producer Magazine*. March. http://www.ethanolproducer.com/article.jsp?article_id=5345.

Volvo website (2010) Volvo Bio-DME Unique Commercial Test Operations, 2010-2012, <http://www.volvotrucks.com/SiteCollectionDocuments/VTC/Corporate/News%20and%20Media/publications/Volvo%20BioDME.pdf>

Walsh, M. (2008) "U. S. cellulosic biomass feedstock supplies and distribution." July 30. <http://ageconsearch.umn.edu/bitstream/7625/2/U.S.%20Biomass%20Supplies.pdf>.

Wang, M. and Haq, Z. (2008) Letter to Science about Searchinger et al. article. March, http://www.transportation.anl.gov/pdfs/letter_to_science_anldoe_03_14_08.pdf.

Ward, P. and Teague, J.M. (1996) Fifteen Years of Fuel Methanol Distribution. California Energy Commission report # CEC-999-1996-017.

Waterland, L. (2006) California Alternative Fuels Market Assessment. CEC-600-2006-015-D.

Waynick, J.A. (2005) Characterization of Biodiesel Oxidation and Oxidation Products. Task 1 Results. Final report by the Southwest Research Institute for the Coordinating Research Council Project No. AVFL-2b, August.

Westcott, P.C. (2007) Ethanol Expansion in the United States, How Will the Agricultural Sector Adjust? USDA Report, FDS-07D-01.

Westervelt, A. (2010) "Algae Emerges as DOE Feedstock of Choice for Biofuel 2.0." *SolveClimate*.

White, M. G., and R. Hernandez (2007) Final Report – Production of Diesel Components and Propane from the Catalytic Cracking of Biocrude Components. [http://www.propanecouncil.org/uploadedFiles/REP_12335%20BioPropane%20from%20Syngas%20and%20Glycerides\(1\).pdf](http://www.propanecouncil.org/uploadedFiles/REP_12335%20BioPropane%20from%20Syngas%20and%20Glycerides(1).pdf)

Whoriskey, Peter (2009) "The Hydrogen Car Gets Its Fuel Back." Washington Post, October 17.

Winter, A. (2009) "'EPA Signals Support for Higher Ethanol Blends but Delays Decision'." New York Times. December 1. <http://www.nytimes.com/gwire/2009/12/01/01greenwire-epa-signals-support-for-higher-ethanol-blends-75721.html?scp=1&sq=epa%20signals%20support%20for%20higher%20ethanol&>

Williams, R. B., Jenkins, B. M., and Kaffka, S., (2008) Draft Report, An Assessment of Biomass Resources in California, March, Prepared for CEC under contract 500-01-016

Williams, R. and Gildart, M. (2007) "California Biomass Reporting System," database from California Biomass Collaborative and California Energy Commission, Davis, CA, <http://biomass.ucdavis.edu/tools.html>.

Whitford, D. (2010) Building the World's Longest Ethanol Pipeline. Fortune Magazine, March, http://money.cnn.com/2010/03/11/news/companies/ethanol_pipeline.fortune/

Wipke, K, Sprik, S. Kurtz. J. and Ramsden, T. (2009) "Controlled Hydrogen Fleet Infrastructure Demonstration and Validation Project Fall 2009, Composite Data Products, Final Version September 11, 2009", Technical Report NREL/TP-560-46679

Wisner, R. (2008) "Impact of Biofuels on Corn and Soybean Prices." Agricultural Marketing Resource Center Renewable Energy Center.

World Bank (2008) Biofuels: The Promise and the Risks. World Development Report. pp. 70-71. http://siteresources.worldbank.org/INTWDR2008/Resources/2795087-1192112387976/WDR08_05_Focus_B.pdf, 2008

Xu B., Liu, X., Haubrich J. and Friend C.M. (2009) Vapour-phase gold-surface-mediated coupling of aldehydes with methanol [Journal]. Nature Chemistry, 2. pp. 61 - 65.

Xuan, J, Leung, M. K. H., Leung, D. Y. C., Ni, M. (2009) "A review of biomass-derived fuel processors for fuel cell systems", Renewable and Sustainable Energy Reviews 13: 1301–1313

Yborra, Stephen C. (2007) "Roadmap for Development of Natural Gas Vehicle Fueling Infrastructure And Analysis of Vehicular Natural Gas Consumption by Niche Sector," p 2. A report by CVEF to the Department of Energy.

You, Y., et al. (2008) "Economic Cost Analysis of Biodiesel Production: Case in Soybean Oil." Energy & Fuels, vol. 22, no. pp 182–189.

Zhang, Y., Joshi, S., and MacLean, H.L. (2010) Can ethanol alone meet California's low carbon fuel standard? An evaluation of feedstock and conversion alternatives. Environ. Res. Lett. Vol. 5, 014002.

Zhang, Y., Dub, M. A. McLean, D.D., and Kates, M. (2003) "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis." (Bioresource Technology) 90, no. pp 229–240.

Appendix A. Schematics of a Wet Mill and Dry Mill Ethanol Process

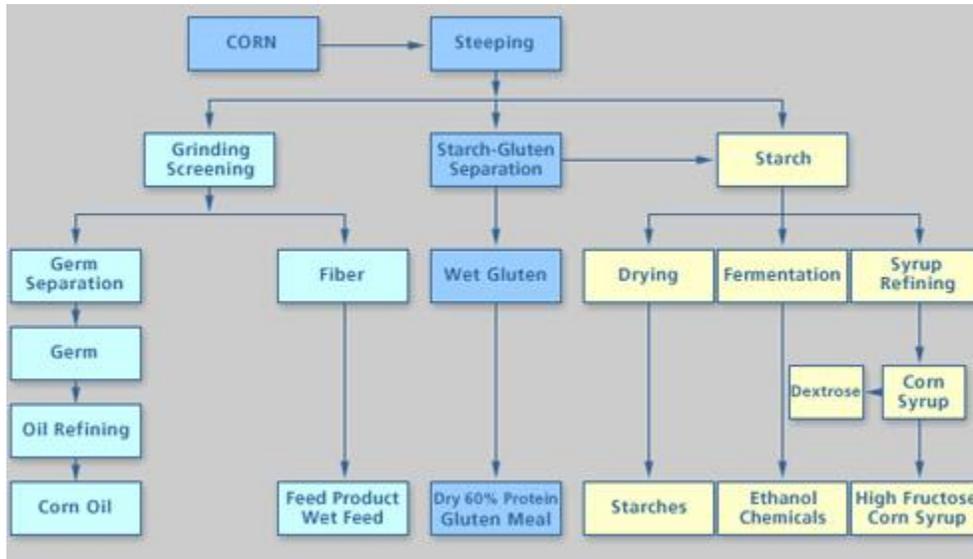


Figure A-1: Wet Mill Ethanol Process Schematic (Source: Renewable Fuels Association)

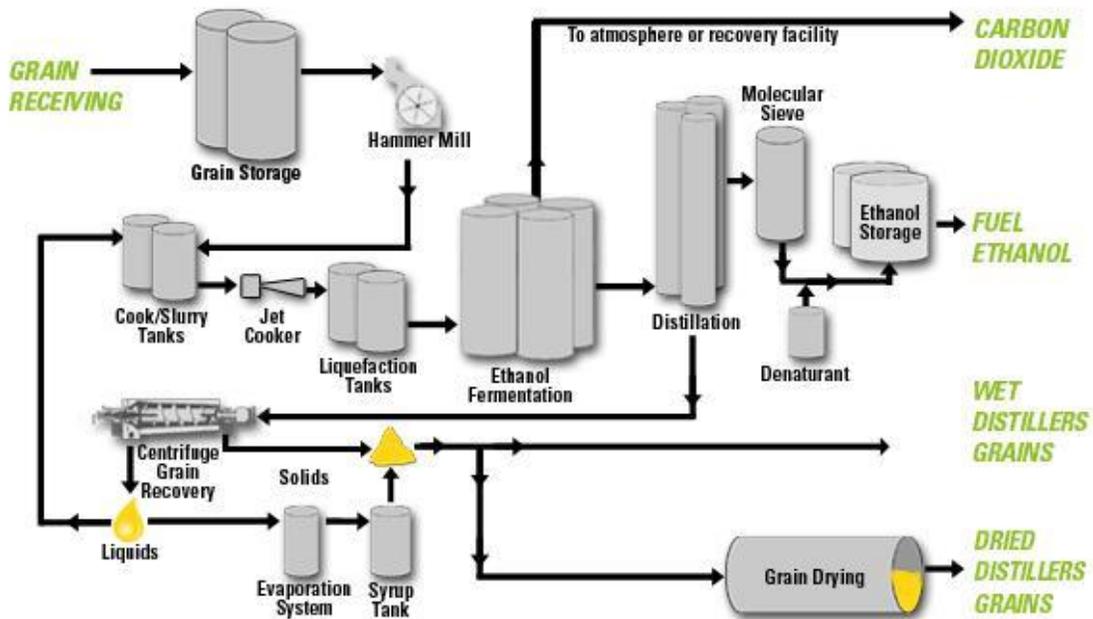


Figure A-2: Dry Mill Ethanol Process Schematic (source: ICM, Inc. (www.imcinc.com))

Appendix B. Irrigation Requirements for Various Crops in Various Regions in California

Table A-1: Applied Irrigation Water in acre-foot per acre for the 10 California Hydrologic Regions in 2001

No.	HR_Name	G	R	C	SB	Cn	DB	Sf	O	A	P	TP	TM	M	OG	Po	OT	AP	OD	ST	V
01	North Coast	0.93	0.00	0.00	0.00	1.79	0.55	0.00	1.90	3.23	2.65	0.00	0.00	1.05	3.04	2.54	1.88	0.00	3.18	2.57	0.86
02	San Francisco Bay	0.88	0.00	0.00	0.00	2.20	1.55	1.04	2.96	4.43	4.72	3.19	0.00	1.27	2.00	0.00	2.11	0.00	3.47	2.84	1.23
03	Central Coast	0.93	0.00	0.00	0.00	1.79	1.48	1.43	2.85	4.46	3.45	2.50	2.20	1.16	3.02	3.40	1.85	4.20	2.88	2.18	1.64
04	South Coast	1.33	0.00	0.00	0.00	1.94	1.54	0.00	1.65	4.89	4.51	2.00	1.84	1.23	1.48	2.06	1.96	3.44	3.36	3.26	1.19
05	Sacramento River	1.27	5.89	3.26	0.00	3.09	2.41	0.79	2.44	4.80	3.85	3.31	3.23	1.60	3.81	0.00	2.99	3.58	3.81	2.51	1.70
06	San Joaquin River	1.28	5.58	3.14	2.11	2.76	2.43	1.58	2.93	5.17	5.07	3.15	2.52	2.56	3.64	3.49	1.87	3.52	3.76	3.06	2.08
07	Tulare Lake	1.68	0.00	3.13	2.91	3.48	2.74	1.69	3.06	5.15	4.93	2.58	2.50	2.41	3.24	2.36	1.64	3.83	3.91	3.33	2.60
08	North Lahontan	1.92	4.52	0.00	0.00	0.00	0.00	0.00	0.00	3.65	4.65	0.00	0.00	0.00	3.01	2.18	2.34	0.00	0.00	0.00	0.00
09	South Lahontan	2.00	0.00	0.00	0.00	2.69	0.00	0.00	2.83	6.45	5.74	0.00	0.00	3.11	3.39	4.12	3.56	5.21	5.27	5.19	2.29
10	Colorado River	2.38	0.00	5.34	5.38	3.00	2.70	0.00	2.97	6.55	6.29	3.09	2.81	3.66	3.50	4.12	3.52	0.00	5.38	5.29	2.40
HR = Hydrologic Regions; G = Grain = Wheat, barley, oats, miscellaneous grain and hay, and mixed grain and hay																					
R = Rice and wild rice; C = Cotton; SB = Sugar beets; Cn = Corn (field and sweet); DB = Dry Beans; Sf = Safflower																					
O = Other = Flax, hops, grain sorghum, sudan, castor beans, miscellaneous fields, sunflowers, hybrid sorghum / sudan, millet and sugar cane																					
A = Alfalfa and alfalfa mixtures																					
P = Pasture = Clover, mixed pasture, native pastures, induced high water table native pasture, miscellaneous grasses, turf farms, bermuda grass, rye grass and klein grass																					
TP = Tomatoes for processing; TM = Tomatoes for market; M = Melons, squash and cucumbers; OG = Onions and garlic																					
Po = Potatoes																					
OT = Other Truck = Artichokes, asparagus, beans (green), carrots, celery, lettuce, peas, spinach, flowers nursery and tree farms, bush berries, strawberries, peppers, broccoli, cabbage, cauliflower and brussel sprouts																					
AP = Almonds and pistachios																					
OD = Other Deciduous = Apples, apricots, cherries, peaches, nectarines, pears, plums, prunes, figs, walnuts and miscellaneous deciduous																					
ST = SubTropical = Grapefruit, lemons, oranges, dates, avocados, olives, kiwis, jojoba, eucalyptus and miscellaneous subtropical fruit																					
V = Vine = Table grapes, wine grapes and raisin grapes																					

