

**Biofuels for Transportation:  
Current Status and Future Opportunities**

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## Executive Summary

High consumption of petroleum is associated with a number of problems such as climate change and air pollution which are directly tied to heavy use of fossil fuels. While substituting petroleum in other sectors has a number of alternatives, it is particularly challenging to find substitutes for petroleum in transportation. Biofuels – fuels derived from biomass feedstock – have the potential to replace petroleum while satisfying three principal problems; climate change, air quality and need for fuel from domestic sources. The reason that biofuels are attractive alternative transportation fuels are expectations that:

- Biofuels can positively affect climate change because a decreased amount of carbon dioxide and other greenhouse gases (GHGs) is expected from biofuels
- Biofuels can be produced domestically, alleviating dependence on foreign sources,
- Burning biofuels emits lower levels of criteria pollutants leading to improved air quality.

In this paper we provide a review of the status of biofuels and assess the opportunities for biofuels as alternative transportation fuels. The paper reviews the biofuels currently available and evaluates the development and future potential of the next generation biofuels. We categorize biofuels into three groups based on the feedstock and/or process involved, and the place on the development and commercialization timeline. The three groups are:

- *First generation biofuels* – for example ethanol from sugar cane or corn, biodiesel. These fuels are currently available but may compete with food sources. Chemical composition is very different than conventional fuels so integration may also be an issue.
- *Second generation biofuels* – for example lignocellulosic ethanol, Fischer-Tropsch fuels, synthetic diesel, biomethane. These fuels are in development at pilot scale level, and are derived from non-food sources and waste biomass. Chemical composition may be very different than conventional fuels.
- *Advanced biofuels or third generation biofuels* – for example algae-based fuels, use of novel enzymatic pathways. These fuels are mostly in research and development phases. They rely on completely new feedstock sources or production processes. They have a composition that is very similar to current fossil fuels but cleaner and with a much smaller carbon footprint.

Within these three groups are five types of fuels examined in this paper: alcohol fuels, biodiesel and renewable diesel, synthetic fuels and dimethyl ether, biogas or biomethane, and advanced biofuels. Each type of biofuel is reviewed addressing the properties and definition of each, the principal sources and production pathways, and the uses in transportation.

*Alcohol fuels* are most widespread now, in particular ethanol. These are fuels mostly for gasoline engines and can be mixed with gasoline in different proportions. The main advantages are they improve fuel economy of vehicles and lower the emissions of certain pollutants. The disadvantages are the overall GHG emissions from current pathways of production, and higher emissions of certain ozone forming contributors (aldehydes and NO<sub>x</sub>). The current vehicle fleet is not optimized for operating on alcohols.

*Biodiesel and renewable diesel* are diesel fuel substitutes derived from plant and animal oils/fats but refined through very different processes, leading to different final products. In the US, biodiesel is derived mainly from soybean oil and has a composition different than diesel fuel. Renewable diesel is derived from a variety of animal waste oils and is more similar to diesel fuel. Biodiesel is currently more available than renewable diesel. The main benefits of these fuels are they can be easily mixed with petroleum-based diesel and provide reductions in tailpipe emissions, with the exception of NO<sub>x</sub>. Disadvantages are lower GHG reductions and petroleum displacement.

*Synthetic fuels - F-T fuels and dimethyl ether* have as a primary advantage the fact that they can be derived from a number of different feedstocks and can be designed with specific performance properties in mind. However, such flexibility makes them expensive, particularly if the starting feedstock is biomass. The other significant advantage is major reductions in emissions by eliminating the sources of soot forming components. The primary disadvantage is that synthetic fuels require modifications to the vehicle delivery system making them harder to integrate.

*Biogas and biomethane* (the cleaned-up final product) is identical to natural gas and provides all the clean fuel properties for which natural gas is known. The primary benefit of biomethane is using waste streams, agricultural or municipal, as the feedstock. The process captures gases that would otherwise be directly contributing to climate change. The primary disadvantage is that biomethane is a gaseous fuel requiring modifications to the existing mainstream vehicle fleet and distribution system. Biomethane can integrate easily with natural gas infrastructure.

*Advanced biofuels* are targeted at eliminating the disadvantages of current first and second generation biofuels. The composition of advanced biofuels is similar to fossil fuels, making integration with vehicles and distribution systems seamless. Advanced biofuels employ algae or specialty enzymes and processes that are radically different from existing biofuel production.

In reviewing the suite of biofuels, their feedstock sources, process pathways, and applicability as transportation fuels, the following broad conclusions were made:

- Multiple feedstocks can be used to derive the same biofuel
- Different processes can be used to derive different biofuels from the same feedstock
- The feedstock and the process pathway are important to understand when evaluating the overall benefits of the biofuel, especially for GHG reductions
- Introducing biofuels to the current vehicle fleet provides limited benefits

- To obtain the greatest benefits, biofuels must be paired with engines and vehicles that are modified to take advantage of the biofuel properties
- Agricultural and land use impact are relevant for biofuels but can be decreased in pathways that use waste organic matter
- Pathways that use waste organic matter – examples include biomethane and DME via waste wood pathway, have minimal land use impacts and offer excellent strategies for reducing GHG emissions.

Within this study we developed a rating scale to help evaluate and compare the different biofuels. We used three main criteria – air quality, climate change, and energy security – and added a few other that are specifically related to transportation, such as distribution of fuel and vehicle modification. In total, the following criteria were used to evaluate a range of biofuels:

- Criteria pollutants
- Petroleum reduction
- Greenhouse gas impact
- Distribution
- Vehicle modifications
- Land use effects

We relied on available data from literature to derive quantitative data for this rating. The rating system was based on a scale from 1 to 5 for each criterion. The total maximum number of points was 30; the higher the number, the better the rating of the fuel. Our analysis provided the following ratings for the biofuels examined:

Ethanol (E10, E85)	14-16
Biodiesel (B20)	18
Renewable Diesel (RD30)	20
Synthetic Diesel	23-26
Dimethyl ether (DME)	22
Biomethane	20-28

The analysis shows that current biofuels such as ethanol and biodiesel have lower ratings than synfuels and biomethane. Alcohol fuels provide a good introductory pathway and learning for all biofuels but are not a likely long-term solution. Biomethane positively effects GHG emissions and criteria pollutants and is an excellent choice for a transportation fuel.

First generation biofuels, like ethanol and biodiesel, offer limited benefits as alternative fuels - limited displacement of petroleum and limited improvement in emissions. Greatest uncertainty is regarding GHG effects of first generation biofuels. However, we believe that their use offers important learning and should be considered a transition phase in further development and use of biofuels.

Second generation biofuels use a more diverse biomass feedstock and provide significant improvements in vehicle emissions and GHG benefits. When they use waste material as feedstocks, they provide an excellent solution in terms of GHG benefits. However, the production pathways for these fuels are generally energy intense and thus expensive, as is the example with synfuels and DME, or their use is somewhat limited currently due to the need for greater infrastructure and/or vehicle modifications (e.g. biomethane). We believe that use of synfuels and biomethane can be excellent alternative fuels and should be deployed and developed further regionally or in certain niche markets. Specifically, for regions or markets that have a high concentration of natural gas vehicles, such as transit buses, the choice of biomethane as an alternative fuel is excellent. Another niche market for biomethane is agricultural regions with high concentration of waste biomass as feedstock where the biomethane can be generated and used on-site.

Third generation or advanced biofuels are currently in research and development stage and farther from commercialization. Their attraction is that they offer to bypass or eliminate the problems listed for first and second generation biofuels by employing completely new production pathways, or use of algae or dedicated crops as feedstocks.

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## Abbreviations, Acronyms, and Formulas

ASTM – American Society for Testing and Materials  
B20 – Diesel-biodiesel blend with 20 percent biodiesel  
B30 – Diesel-biodiesel blend with 30 percent biodiesel  
BTL – Biomass-to-liquids  
Btu – British thermal unit  
CH<sub>4</sub> - Methane  
CO – Carbon monoxide  
CO<sub>2</sub> – Carbon dioxide  
CTL – Coal-to-liquids  
DME – Dimethyl ether  
DOE – Department of Energy  
EIA – Energy Information Administration  
EPA – Environmental Protection Agency  
E10 – gasoline-ethanol blend with 10 percent ethanol contents  
E85 – gasoline-ethanol blend with 85% ethanol  
FAME – fatty acid methyl esters  
F-T – Fischer-Tropsch  
GHG – Greenhouse Gases  
GTL – Gas-to-liquids  
HC – Hydrocarbons  
H<sub>2</sub>S – Hydrogen sulfide  
IEA – International Energy Agency  
LPG – Liquefied petroleum gas  
MTBE – Methyl tertiary butyl ether  
NO<sub>x</sub> – oxides of nitrogen  
PM – particulate matter  
ULSD – Ultra low sulfur diesel

# 1. Introduction – need for alternative fuels for transportation

Fossil fuels, coal, petroleum and natural gas, have been an integral part of the world economy and have been used in all the different sectors. Coal originally replaced use of wood for residential and process heat especially during industrial revolution. Introduction of petroleum replaced coal as a more convenient source for industrial processes and enabled the rise of transportation. Some sectors of the economy have flexibility in terms of the fuels source they use; for example, the industrial and electricity sector can use coal, oil or other sources. Transportation however is unique in this respect that it relies nearly exclusively on liquid fossil fuels. The chart in Figure 1 shows that petroleum consumption in the US is dominated by the transportation sector, which uses close to 70% of petroleum consumed in the US.

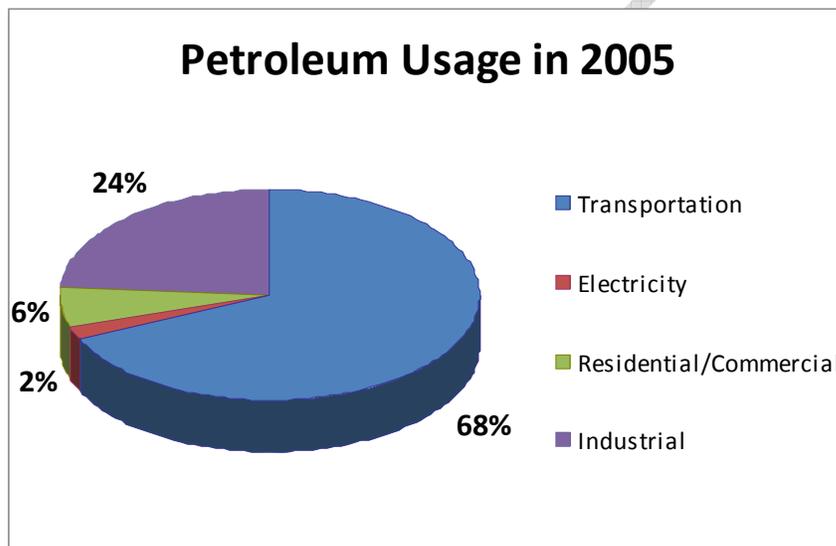


Figure 1: Petroleum consumption in the US by sector (Source: Annual Energy Outlook, 2007, EIA)

The high consumption of petroleum is associated with a number of problems. First is the problem of climate change and greenhouse gases which are directly tied to heavy use of fossil fuels. Combustion of fossil fuels leads to accumulation of carbon dioxide in the atmosphere causing and contribution to global climate change problems. Intergovernmental Panel on Climate Change (IPCC) states with 98% certainty the anthropogenic causes of observed climate change effects which include habitat loss, melting of ice caps, and changing weather patterns. Second is the need for greater energy independence and reliance on domestically produced fuels over imported ones. More than half of petroleum used in the US is currently imported with the trend toward even larger imports in the future. Third are local air quality problems such as smog that are created by burning petroleum in the current vehicle fleet. Air pollution leads to increased respiratory diseases such as asthma, affects growth rates of children, and may contribute to increased cancer rates.

The three, above mentioned, reasons are the primary driving forces to move away from petroleum in transportation and seek alternative fuels. An interesting alternative option to petroleum fuels are biofuels – or fuels derived from biomass feedstocks. What makes biofuels attractive is that they may have the potential to address the three principal problems associated with petroleum fuels. It is expected that:

- Biofuels can positively affect climate change because a decreased amount of carbon dioxide and other greenhouse gases (GHGs) is expected from biofuels
- Biofuels can be produced domestically, alleviating dependence on foreign sources,
- Burning biofuels emits lower levels of criteria pollutants leading to improved air quality

Biofuels present a new and interesting alternative to fossil fuels but a deeper understanding of the sources, process and uses of biofuels is required in evaluating their potential and the role they will play in the short and long term as alternatives to petroleum in the transportation sector.

## **2. Scope of paper**

The scope of this white paper is to provide a review of the status of biofuels, and to assess the opportunities for biofuels as alternative transportation fuels based on the satisfaction of the three main criteria – climate change, energy security, and air quality benefits. Since the field of biofuels is rapidly changing and developing, the scope of the paper is to review the biofuels currently available as well evaluate the development and potential of the next generations of biofuels.

The approach used in this white paper was to review each biofuel type in three stages by covering its:

- properties,
- processes used in biofuel production, and
- uses as transportation fuel.

Based on the review, we selected six principle evaluation criteria to do a side-by-side comparison of different biofuels. The comparative evaluation together with the review of each biofuel type provides a basis for a set of recommendations regarding the short-term and long-term roles for biofuels as transportation fuels.

## **3. Overview of biofuels**

The definition of a biofuel is a fuel whose source is derived from biomass material which includes all substances of biogenic origin including plants (or parts of plants), animals, and their byproducts such as manure and dung. Generally biofuels are grouped into two

basic categories (with a third just emerging) depending on the feedstock and/or the process involved:

- *First generation biofuels* – are derived from the sugar, starch, or oil of grains and vegetable crops and are commercially available. In this case only a small part of the feedstock is used. Examples include ethanol from sugar cane or corn starch, or biodiesel from soybean oil. These feedstocks can compete for production of food crops.
- *Second generation biofuels* – refers to biofuels derived from lignocellulosic biomass, or organic portions of municipal solid waste or via a thermochemical conversion (gasification or Fischer-Tropsch processing). The advantages are that this biomass feedstock is more abundant and inexpensive and that the total biomass is used in the process. In terms of commercialization the second generation biofuels are at the pilot plant scale.
- *Advanced biofuels or third generation biofuels* – emerging as a new category to include nascent methods of production such as use of new enzymes, microorganisms, and new feedstock such as algae and dedicated energy crops to produce biofuels. They also include dedicated “energy crops” such as perennial grasses and fast growing trees. Further research and development is needed in order to bring the advanced biofuels to market.

Regardless of feedstock, a key challenge is converting biomass components into fuels that can be used in vehicle engines (combustion engines) and that would have similar properties to petroleum-based fuels in terms of performance. Biomass is rich in *carbohydrates* - sugars, starch, and cellulose. Sugars are very simple, and starch and cellulose are more complex carbohydrates consisting of long chain polymers rich in oxygen. In contrast, petroleum-based fuels such as gasoline and diesel consist mostly of *hydrocarbons* and contain much less oxygen. The challenge is finding processes and solutions that convert long chain carbohydrates into shorter hydrocarbons while minimizing loss of energy.

Currently, the two main pathways of biomass conversion are biological and thermochemical. The biological processes involve enzymes. In step one, enzymes break apart the cellulose and starch to simple sugars. In step two, the sugars are converted via fermentation into alcohols. Thermochemical conversion also requires two steps. The first step is heating in the presence of a catalyst to break apart the large molecules into single molecules. In the second step the smaller molecules are recombined into the desired molecule (alcohol, diesel, gasoline, etc.). Each method is not without drawbacks. The biological process is relatively slow while the thermochemical process is energy intensive with high energy losses.

In Chapters 4 and 5 we review the first generation biofuels – alcohol fuels, biodiesel and renewable diesel. Chapters 6 and 7 provide a review of second generation fuels – synthetic fuels (Fischer-Tropsch liquids), dimethyl ether, and biogas and biomethane.

Advanced or third generation biofuels are reviewed in Chapter 8. In Chapter 9 we evaluate and compare the biofuels using a rating system that we created based on a list of criteria. We then provide some conclusions and recommendations based on the review and evaluation of biofuels presented.

## **4. Alcohol Fuels –ethanol, methanol, and butanol**

Alcohol fuels are liquids that can be used as transportation fuels, either pure or blended with petroleum. There are principally three alcohols in use or being considered as transportation fuels - methanol, ethanol, and butanol. Ethanol, otherwise known as “grain alcohol” is currently of most interest while methanol has a history of issues related to its toxicity and butanol is not yet available in sufficiently high production quantities.

Alcohols are considered renewable fuels when generated from renewable biomass feedstock. The source of the feedstock and the process by which alcohols are produced may vary. However, regardless of the process and feedstock, the properties and uses of alcohol fuels are identical, so we first examine those in some detail in the following two sections. Since a good overall understanding of the fuel requires understanding the feedstock source and the process used to generate the fuel, a separate section is dedicated to examining the different feedstocks and production processes. This is especially important in understanding the long-term sustainability of the fuel being considered.

### **4.1 Definitions and properties of alcohols as fuels**

Alcohols are clear, colorless liquids that burn well in internal combustion engines. They are derivatives of simple hydrocarbons and are chemically much simpler than gasoline. Methanol is a derivative of methane, ethanol of ethane and butanol of butane. Chemical formulas for each of the three alcohols and more details on the properties of alcohol fuels in comparison to gasoline are available in Appendix A.

Alcohols have generally lower heating values compared to gasoline and higher solubility in water. The lower heating value means that a larger volume of alcohol fuel is needed to deliver the same amount of energy as a gallon of gasoline. For example, a gallon of pure ethanol (E100) contains 34% less energy than gasoline. Methanol’s energy content is half that of gasoline and butanol’s is very close to that of gasoline. As a result, for each gallon of gasoline a larger amount of ethanol is needed than methanol or butanol. An advantage of alcohols are higher octane numbers allowing it to burn more smoothly in a spark ignition engine (smaller tendency to cause “engine knock”). High octane numbers of alcohols are the reason they are commonly added to gasoline as octane boosters.

The solubility of alcohol in water is a drawback that alcohol fuels have, in particular ethanol, because extra effort has to be made in order to remove water from the alcohol fuel. Butanol, if it becomes commercially available, will be more easily transported as butanol is less soluble in water.

## 4.2 Principal sources, production processes and pathways

### Ethanol

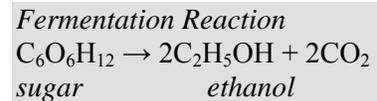
All ethanol is the same but the feedstock sources and process are different. Ethanol can be produced from feedstock that contain sugar or material that can be converted to sugar such as starch and cellulose. There are at the moment three categories of feedstocks for ethanol:

1. Sugar feedstock – sugar beet or sugar cane
2. Starch feedstock – corn, wheat, and barley starch
3. Lignocellulosic feedstock – grasses, forestry, and crop residue

The current majority of the ethanol in the United States is corn ethanol, or more precisely derived from corn starch. By contrast, Brazilian ethanol is sugar cane ethanol. The processes associated with each feedstock differ in complexity. We emphasize here that the starting material will define the necessary conversion steps and choice of processes required to produce the alcohol fuel. For example, it is much simpler to convert the sugars to alcohol, followed by starch and finally grasses and crop residues. We review the basics of each of the conversion processes below.

#### Sugarcane and Corn Ethanol

The principal method of producing ethanol from sugars is by fermentation using enzymes from yeast. During fermentation, half of the sugar is converted to ethanol and the other half is released as carbon dioxide (CO<sub>2</sub>).



The conversion process is fairly straightforward when the starting material is sugar. Sugarcane contains about 30% of soluble sugar which is easily extracted and then fermented. When the starting feedstock is corn grain (or another starchy grain such as wheat or barley) the process requires more steps. First, the starch has to be isolated (by wet or dry milling) which is then followed by treating with enzymes and acids (hydrolysis) to separate the sugar which then goes to a fermentation step (Huber, Iborra and Corma, 2006). The diagram in Figure 2 shows the different processing steps when starting from corn or from sugarcane. The additional steps when starting with grains rather than sugar feedstock make this process even more complicated and expensive.

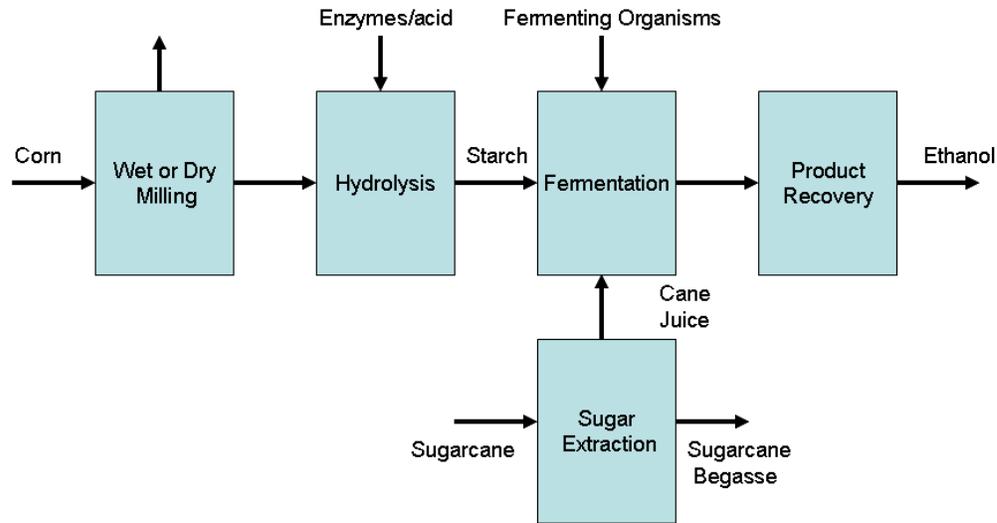


Figure 2: Flow diagram for ethanol production from sugar cane and corn (Adapted from: Huber et al, 2006)

### Cellulosic Ethanol

Cellulosic ethanol refers to ethanol that is derived from lignocellulosic material such as grasses, wood and wood chips, and agricultural residues such as wheat and rice residues. These feedstocks are collectively called lignocellulosic or cellulosic biomass reflecting the mixture of complex material naturally found in all woody plant matter - cellulose, hemicellulose, and lignin. The percentage of these components in grasses, agricultural residues and wood chips is shown in Figure 3.

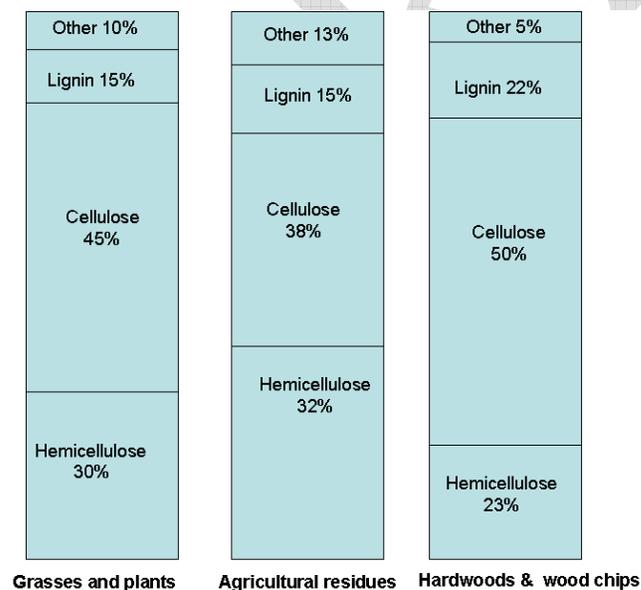


Figure 3: Composition of cellulosic feedstock (Source: Wyman et al, 1993)

Brief definitions of cellulose, hemicellulose, and lignin are:

- *Cellulose* is a crystalline polymer consisting predominantly of glucose sugars
- *Hemicellulose* coats the cellulose and is a complex amorphous polymer consisting predominantly of xylose sugars.
- *Lignin* is a complex organic polymer found in woody plants and is the non-active part in ethanol production

Cellulose and hemicellulose are the parts of the plant that contain sugars which can be extracted and converted to ethanol. Lignin on the other hand is a non-active component but can be used to provide the process heat. The two sugars most useful for conversion to ethanol are glucose and xylose and they are bound firmly to the cellulose and hemicellulose. They are not easily separated from the original plant matter, unlike sugars from corn and other starchy biomass, and involve more complicated and expensive extraction steps.

There are two pathways of producing cellulosic ethanol from biomass; the first is biochemical and the second is thermochemical. The biochemical pathway depends on separating the sugars from the cellulose and hemicellulose. The thermochemical pathway does not attempt to separate the sugars but partially decomposes the entire starting feedstock to much smaller building blocks that are thereafter recombined to produce ethanol. Each pathway is analyzed in more detail below.

#### Cellulosic ethanol - Biochemical pathway

This process consists of hydrolysis and fermentation using chemicals, enzymes, and fermentation microorganisms. Hydrolysis is the breaking down hemicellulose and cellulose (or generally any complex polymer) to smaller components in the presence of water and enzymes and/or acids. If an acid is used, then the process is called “acid hydrolysis” and if an enzyme is primarily used then it is called “enzymatic hydrolysis.”

Pre-treating the biomass with hot acid partially hydrolyzes the hemicellulose and separates the lignin. The soluble fraction (xylose) is separated and fermented to produce ethanol. The insoluble cellulose part is treated again with acids and enzymes to glucose which is then fermented to ethanol. The diagram of this process is shown in Figure 4.

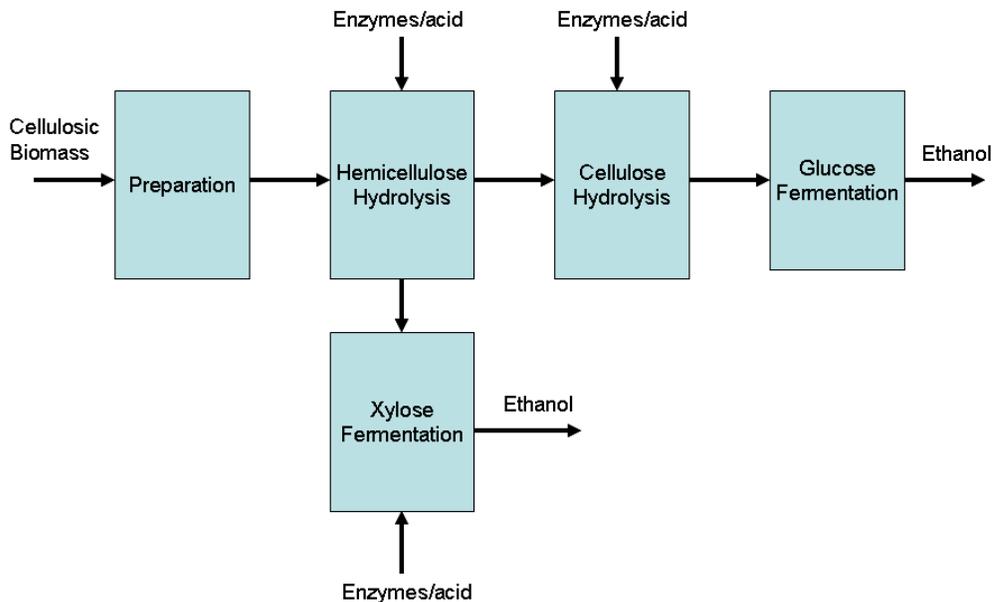


Figure 4: Diagram for biological conversion of cellulosic biomass to ethanol (Source: Wyman et al, 1993)

The biochemical pathway requires selection and development of enzymes that can efficiently break apart the cellulose allowing the sugar to be accessed. The main drawback of the biochemical process is that it is relatively slow and thus can not produce high yields at this time. In comparison, the thermochemical pathway is a faster process which is why at the moment most of the cellulosic ethanol is produced using the thermochemical route.

#### Cellulosic Ethanol – Thermochemical pathway

Thermochemical processes, as the name suggests, involve heat and chemicals (or biochemicals) to convert biomass feedstock to ethanol. The first step in this pathway is gasification (to produce synthesis gas) followed by a second step which can be:

- a) biochemical reaction – fermentation using enzymes, or
- b) catalytic reaction – recombination reaction using catalysts.

The attraction of the thermochemical pathway is that it converts and uses all the parts of the starting feedstock which can now be more easily converted to ethanol. The first step, gasification of the feedstock to synthesis gas, or syngas (CO and H<sub>2</sub>) converts the starting carbon-rich material by heating it at high temperatures with controlled amounts of oxygen. It is an efficient way of extracting energy and breaking apart the original material to simple compounds. In the next step, the syngas is fermented in a bioreactor using enzymes to produce ethanol. An example of this pathway is presented in Figure 5.

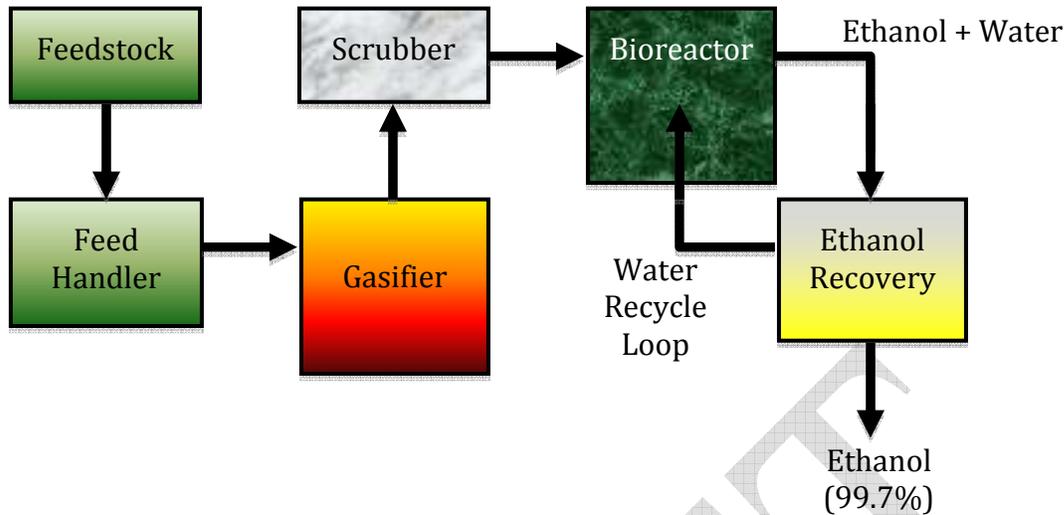


Figure 5: Thermochemical production of ethanol.

The thermochemical pathway maximizes the use of the feedstock and is flexible in terms of the starting feedstock quality. The drawback is that main step in this process, gasification, is fairly energy intensive which not only adds to the cost but affects the overall energy balance of ethanol production. The second step, catalytic or enzymatic conversion, requires special catalysts or enzymes which are unique and expensive at the moment. These cost and energy requirement challenges need to be overcome for cellulosic ethanol to become cost competitive and therefore, commercially viable.

#### Development and commercialization projects

The number of companies involved in cellulosic ethanol production has been growing in part spurred by the funding from Department of Energy (DOE). For example, in 2007 DOE funded pilot plant projects for cellulosic ethanol production involving the following companies and projects (DOE, 2007):

- Abengoa Bioenergy Biomass of Kansas – thermochemical and biochemical processing of corn stover, wheat straw, and switchgrass
- Alico, Inc. – gasification of agricultural residues and fermentation of syngas
- Range Fuels, Inc. – gasification followed by catalytic upgrading of syngas to ethanol and methanol
- Iogen Biorefinery Partners, LLC – agricultural residues
- Broin Companies – production of cellulosic ethanol from corn fiber and stover
- BlueFire Ethanol – acid processing of green and wood waste followed by fermentation

The goal of the DOE efforts is to make cellulosic ethanol cost competitive to gasoline by 2012. The cost is affected by the feedstock cost and process costs which include energy costs and special enzymes and catalysts. Feedstock costs are dominant for corn ethanol and the 2002 numbers show that it made up 57 percent of the total production cost

(USDA, 2005). Capital costs to build a cellulosic ethanol plant are also higher than for a corn-based plant of similar size. One study estimated that the capital costs for a 50 million gallon per year cellulosic ethanol plant were \$375 million (2005 dollars) as compared with \$67 million for a corn-based plant of similar capacity size (Port, 2005).

While ethanol is the dominant alcohol fuel and most development efforts are focused on ethanol, we present a review of sources and processes for methanol production below.

## **Methanol**

The traditional process for methanol production is steam reforming of natural gas to produce synthesis gas which is then catalytically converted to methanol in stage two of the process<sup>1</sup>. Steam reforming of natural gas is the most efficient process for methanol production today because it avoids the energy intensive gasification step needed for syngas production from other carbon-containing feedstock such as coal or biomass. However, biomass, crop residues, and municipal solid waste are the preferred feedstock for a renewable energy pathway. In this case, the feedstock is first gasified to produce syngas and then converted to methanol. In general, the process will consist of biomass pretreatment, conversion to syngas, syngas clean up, and finally conversion to methanol. While this would provide a renewable source of methanol, it should be noted that gasification is an energy intensive step and can contribute to overall lower efficiencies of the process and greater costs.

Another way of producing methanol is in combination with dimethyl ether (DME), also an alternative transportation fuel. The paper mill industry produces a byproduct, lback liquore, which can then be converted to syngas to be used to produce methanol and DME. Black liquor is the solution that remains after the cellulose fibers (used in paper production) are removed. It consists of hemicellulose and lignin residues mixed with inorganic material from the processing. More on DME is presented in Chapter 6 of this paper.

Finally, a third and very novel method of producing methanol is a one-step and very efficient process proposed by Olah et al. (2006) in producing methanol from natural gas. In the long-term, the authors suggest a selective chemical recycling of carbon dioxide to produce both methanol and DME. The authors propose that this process would enable complete recycling of carbon dioxide which might help reduce greenhouse gas emissions and therefore address the climate change problem.

## **Butanol**

Butanol is currently widely used as an industrial solvent and produced from petrochemical feedstock with a price of \$ 3.75 per gallon. Biobutanol, a renewable

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<sup>1</sup> Current market price of methanol from natural gas is \$1/gallon.

product, can be generated using the same feedstock used for ethanol production. In addition, the same facilities used for ethanol production can be used as the processes are very similar with the exception of requiring different enzymes that ferment the sugars to butanol rather than ethanol.

There are a fewer companies involved in biobutanol processes. BP and DuPont have partnered to produce biobutanol and have built a pilotplant in United Kingdom This project is focusing on the fermentation enzymes and increasing the production yields.

Another company involved in butanol production is a start-up company, Gevo. Gevo is concentrating on non-fermentation pathways using suitable host organisms and is developing a proprietary process technology to convert cellulosic crops and waste into butanol. The butanol could be blended with gasoline but Gevo is also developing a refining process to produces a whole suite of fuels such as jet-fuel, diesel and gasoline.

A third company focusing on butanol is Cobalt Biofuels that recently announced a new round of venture funding. Cobalt is developing a continuous fermentation process, as opposed to more usual batch processes, in combination with genetic engineering. The company hopes to increase the rate of production of biobutanol and decrease the production costs (Cobalt Biofuels, 2008). In all the cases above, the challenge is to produce higher yields of butanol in order to commercialize it.

### **4.3 Uses in transportation of alcohol fuels**

Alcohol fuels are primarily used in gasoline engines (spark ignition engines). Methanol and ethanol can be used as blends or by themselves<sup>2</sup> and butanol can be used only as a blend. Alcohol is present in the fuel market today as a blend with gasoline, as E5 (5% ethanol and 95% gasoline) or E85 (85% alcohol and 15% gasoline). Low level blends up to E10 are called “gasohol.” High level blends such as E85 are available in a limited number of ethanol fueling stations. Ethanol was first introduced to gasoline as a replacement for the additive methyl tertiary butyl ether, better known as MTBE. Due to concerns of MTBE seepage into groundwater supplies, ethanol was mandated as a replacement. The main advantages of blending gasoline with alcohol are:

- Improved engine efficiency by allowing fuel-lean operation (lower fuel-to-air ratio)
- Increased octane number which improves the energy efficiency and fuel economy
- Reduced emissions of carbon monoxide and unburned hydrocarbons.

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<sup>2</sup> Butanol can not be used alone or “neat” in the engine because its melting point is 25.5 °C and at colder temperatures it gels.

Blending alcohol with gasoline has some drawbacks. Alcohol blends have increased vapor pressure causing an increase in evaporative emissions responsible for smog. Evaporation occurs from the fuel system and from the engine exhaust (as partial combustion products) and both will contribute to an increase in local smog concentrations. A group of compounds called aldehydes, generated as byproducts of ethanol combustion in particular have higher emissions. Aldehydes are very reactive compounds and contributors to smog. We note that evaporative emissions peak for a mixtures containing between 5 and 10% ethanol and they decline in blends with a higher percentage of alcohol (Green et al., 2004). With E85 there is a four to five time decrease in evaporative emissions. This is the reason that lower level blends up to E5, or higher level blends as E85 are specifically favored.

The low level ethanol blends can be used in current vehicles without any modification using the existing fueling infrastructure. Ethanol is also available in dedicated ethanol fueling stations providing E85 for flex-fuel vehicles. Flex fuel vehicles are designed to run on gasoline or a blend of up to E85 which provides the user and opportunity to displace gasoline and rely more on ethanol as a fuel. However, there are certain drawbacks to this, that at any given moment of time the exact mixture of ethanol and gasoline in the fuel tank will vary depending on which fuel was used at the filling station. Operating the engine with different fuel mixes means that the engine will not operate in the most optimal state and will not provide the best efficiency of emissions profile. A better approach is to optimize the engine to a particular fuel, something that may be needed as we look at relying more on alternative fuels. A brief review provided by Lotus Engineering of existing engine technologies such as gasoline direct injection and variable compression ratio, shows how engines can be modified to complement use of alternative fuels (Pearson and Turner, 2007).

While ethanol is primarily used as an alternative fuel for spark ignition engines, it can be blended with diesel for use in compression ignition engines (or diesel engines). Low level ethanol-diesel blends have been used as well in urban buses. In Sweden they have tested 15% ethanol-diesel blend with the use of an additive to help improve ethanol solubility in diesel (Larsen et al., 2009). This demonstration shows that alcohols may be able to displace not only gasoline but diesel fuel as well.

Ethanol is, at the moment the alcohol fuel of choice and is commercially available in the United States. In 2007, the United States consumed 6.8 billion gallons of ethanol compared to 139 billion gallons of gasoline (EIA, 2008). However, methanol and butanol can be also used as transportation fuels. Methanol was used as an alternative fuel particularly in California as M85 but was abandoned because it is poisonous and requires extra precautions during handling. As a fuel, methanol is an excellent choice for gasoline engines and for direct-methanol fuel cell vehicles. Methanol does have a long-term potential to replace gasoline and petroleum-based fuels even to provide a basis for a methanol-based economy. Advocates for methanol argue that it has greater advantages, especially compared to a hydrogen-fueled economy (Olah et. al., 2006). To use methanol more widely, the fueling and safety issues would need to be addressed.

Butanol is considered a second generation biofuel and is still under development as a transportation biofuel. There are several advantages of butanol that make it more desirable as a transportation fuel over ethanol:

- Energy content similar to gasoline
- Can be blended at higher concentrations than ethanol in standard vehicle engines
- Less susceptible to separation in presence of water
- Easier distribution through pipelines

The feedstocks are similar to those for ethanol production. However, butanol production is not commercialized yet but developments are underway to bring it to the market as was discussed in the previous section.

### ***Alcohol Fuels***

#### *Advantages*

- *Blend easily with gasoline primarily and with diesel fuel in the presence of additives*
- *Improved engine efficiency and fuel economy*
- *Lower emissions of carbon monoxide and unburned hydrocarbons*

#### *Challenges*

- *Increased emissions of certain ozone contributors (aldehydes)*
- *Lower energy content per gallon compared to gasoline*
- *Some blends have higher NOx emissions*
- *Higher blends can be used only in flex fuel vehicle*
- *Selection of feedstock and process pathway very important*
- *GHG emissions due to land use impacts in question*

## **5. Biodiesel and Renewable Diesel**

Alcohol fuels are alternatives for gasoline, whereas biodiesel and renewable diesel are alternatives for petroleum diesel. In fact, there are three alternative biofuels to petroleum diesel – biodiesel, renewable diesel, and synthetic diesel. Biodiesel is most widely used alternative biofuel for diesel engines and is considered a first generation biofuel. In 2007 the United States consumed 491 million gallons of biodiesel compared to 39 billion gallons of diesel (EIA, 2008). Renewable diesel is a more recent product and is just entering the market. It can be considered a second generation biofuel while synthetic diesel, depending on the feedstock and specific process, is categorized as second generation or advanced biofuel. In this Chapter we discuss biodiesel and renewable diesel. Synthetic diesel will be discussed in Chapter 6.

Biodiesel and renewable diesel are derived from similar feedstocks, animal and plant fats and oils, but each is derived using a different process leading to two quite different products as shown in Figure 6. Biodiesel is an ester, chemically different than diesel, and

is derived by transesterification of fats and oils. Renewable diesel, on the other hand, is chemically very similar to diesel fuel and is derived by hydrotreating fats and oils. More details on the properties, uses and processes for producing biodiesel and renewable diesel are covered in the sections below.

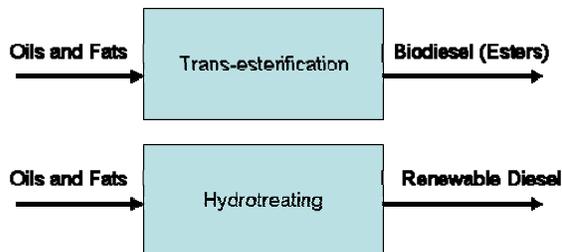


Figure 6: Processes for biodiesel and renewable diesel.

## 5.1 Definitions and properties of biodiesel and renewable diesel

### Biodiesel

Biodiesel consists of esters, or more precisely, fatty acid methyl esters (FAME). It is produced from straight vegetable oils, animal fats and oils, or used cooking oil. The process, called transesterification, transforms fat and oil molecules into smaller ester molecules. The feedstocks are vegetable oils such as rapeseed, soybean, and palm oil but a cheaper alternative today is the use of used cooking oil. The source of the feedstock varies with the geographic region. In the United States for example, biodiesel is derived from soybean oil while in Europe rapeseed oil is the preferred feedstock. It should be noted that the properties of the final biodiesel product will heavily depend on the feedstock it was generated from – animal fats, vegetable and plant oils, recycled greases. We would like to emphasize that biodiesel is not raw or refined vegetable oil or waste cooking oil which if used in the raw state in the engine may actually negatively impact engine durability.

A table listing the chemical and physical properties of biodiesel and renewable diesel is provided in Appendix B. Biodiesel has a separate ASTM standard (D6751), has passed the EPA health-effects testing, and is registered with the EPA as a fuel additive. A good resource on the properties and handling of biodiesel is provided by U.S. Department of Energy publication (DOE, 2006) from which we provide a summary here. Biodiesel is bio-degradable, non-toxic and free of sulfur compounds. It contains about 8% less energy per gallon than a typical No. 2 diesel in the U.S. and has a higher cetane number. Cetane number, similar to octane number for gasoline, defines how well the diesel fuel will perform in a diesel engine. Straight biodiesel may gel and freeze easier than diesel fuel, so precautions have to be used when storing biodiesel.

Biodiesel is not used alone but is blended with diesel - blends of up to 20 percent of biodiesel are common (B20) and in some regions even B30 may be used. Adding

biodiesel has the benefit of improving lubricity of the fuel especially for ultra low sulfur diesel (ULSD) which otherwise has poor lubricating properties.<sup>3</sup> Testing has shown that adding 1% biodiesel can improve lubricity of diesel fuel by as much as 65% (DOE, 2005). Higher blends are not recommended because biodiesel may degrade rubber compounds in hoses and gaskets and dissolve sediments in the fuel system and tank and even degrade some metals and plastics in the fuel system.

## **Renewable diesel**

Renewable diesel, sometimes called non-ester renewable diesel<sup>4</sup> or hydrogenation-derived renewable diesel (HDRD) is derived in a process using vegetable oils and animal fats alone or coprocessed with petroleum in a traditional refinery hydrotreater. At high temperature and pressure, with addition of hydrogen and a catalyst the fats and oils are broken down to mostly paraffinic material, very similar to material found in diesel fuel. The resulting product is a mixture of hydrocarbons that has been reported to meet the ASTM standard for petroleum diesel (D975). Several companies are developing this route. For example, Conoco-Phillips is using hydrotreating to coprocess soy oil and diesel and Neste Oil in Europe is using a bio-only hydrogenation with its NexBTL technology. More detail on different processes can be found in Section 5.2.

Renewable diesel is chemically very similar to diesel. Neste Oil reports that their renewable diesel contains mostly paraffinic hydrocarbons and zero aromatic compounds compared to diesel (Neste Oil, 2006). Because it is chemically similar, it can mix with diesel at any proportion and can be handled just like diesel. This makes renewable diesel very attractive in that it does not require any special transport or storage conditions and can use the existing pipelines and infrastructure. Other valued properties are high cetane number and viscosity similar to diesel.

## **5.2 Principal sources and production pathways of biodiesel and renewable diesel**

### **Biodiesel**

The feedstocks for biodiesel include a variety of animal and vegetable fats and oils as well as recycled restaurant oil. A variety of transesterification technologies can be used where the fat or oil is reacted with alcohol (usually methanol) and a catalyst to produce

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<sup>3</sup> Highway diesel contains up to 500 ppm of sulfur while ultra low sulfur diesel (ULSD) contains less than 15 ppm of sulfur. The US EPA required that all diesel fuel sold in the US be ULSD starting 2006. The removal of the sulfur compounds causes the drop in lubricity of ULSD.

<sup>4</sup> EPA specifically makes the distinction between “biodiesel (mono-alkyl esters)” and “non-ester renewable diesel.” (EPA, final rule on the federal renewable fuel standard (RFS), <http://www.epa.gov/otaq/renewalbefuels/rfs-finalrule.pdf>)

glycerin and methyl esters. The general diagram of a biodiesel production pathway is presented in Figure 7.

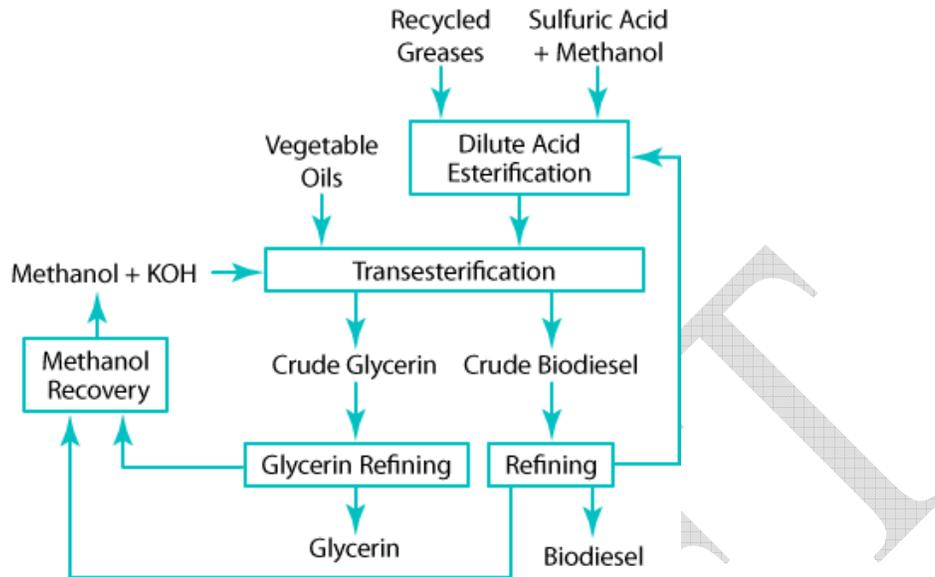


Figure 7: Schematic diagram of biodiesel production path (DOE, 2008)

In United States the principal feedstock for biodiesel is soybean oil, while in the European Union it is rapeseed and sunflower oil. These are also the two largest regions for biodiesel industry currently: the European Union has about 120 plants which in 2005 produced 966 million gallons of biodiesel and the U.S. has about 105 plants (with 70 more under construction) which in 2005 produced 75 million gallons (Stephens, 2007; Schippl et. al., 2007).

## Renewable Diesel

While the feedstocks for renewable diesel are similar to those used for biodiesel, the product and the process are different. Renewable diesel is produced by addition of fats and oils to an existing petroleum refinery hydrotreater process (see Figure 8) or in a stand alone hydrogenation process as shown in Figure 9. As noted earlier, the two companies are investigating renewable diesel extensively; Neste Oil and Conoco Phillips. ConocoPhillips employs an indirect process with the fats and oils added to a petroleum refinery process, whereas Neste Oil uses a direct process in a dedicated plant. The underlying process in both is hydrogenation (addition of hydrogen) of fats and oils at both companies.

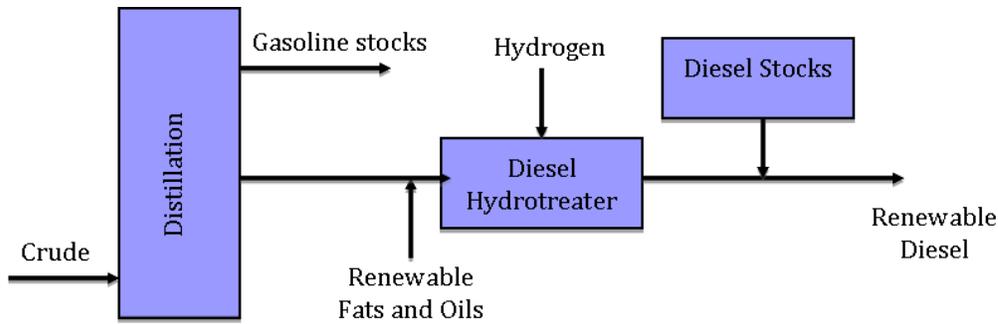


Figure 8: Renewable diesel production process, coprocessed fats and oils in a refinery with petroleum feedstock.

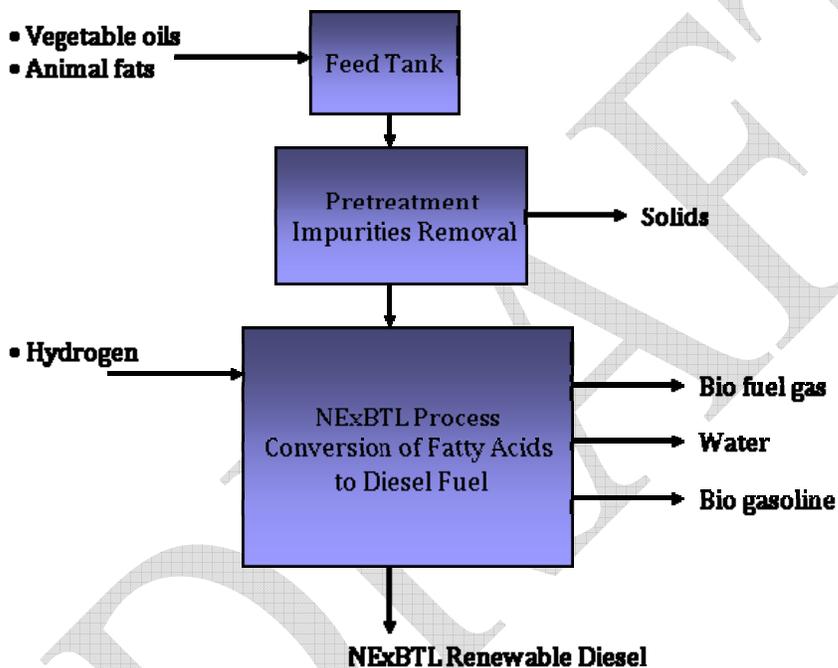


Figure 9: Dedicated renewable diesel process – hydrogenation of fats and oils in NExBTL process.

In addition to the ConocoPhillips and Neste Oil processes presented above, there are several other manufacturers developing and testing production of renewable diesel.

- Petrobras – in Brazil developed the H-Bio process
- Syntroleum - in the US joined with Tyson Foods to produce jet fuel and renewable diesel
- UOP and Eni (Italian oil and gas company) have teamed up to process vegetable oils to renewable diesel.

More description and links to these projects can be found on the DOE website for Alternative Fuels and Advanced Vehicles Data Center ([www.afdc.energy.gov/afdc/fuels/emerging\\_green\\_production](http://www.afdc.energy.gov/afdc/fuels/emerging_green_production))

### **5.3 Uses in transportation – biodiesel and renewable diesel**

#### **Biodiesel**

Biodiesel is easy to use because it blends well with diesel with no special equipment modifications necessary. Most engine manufacturers allow generally use of blends of up to 5% biodiesel and increased number in the U.S. are allowing use of 20% blends (B20) which is popular because it has a good balance of cost, emissions, cold weather performance, and solvency. Up-to-date information on engine manufacturers' position on biodiesel use is compiled by the National Biodiesel Board (National Biodiesel Board, 2008).

Due to lower heating value of biodiesel, using B20 will cause a difference in power, torque, and decreased fuel economy between 1% and 2% depending on the diesel with which it is blended (DOE, Sept 2006). Main advantages of using biodiesel are:

- displacement of petroleum,
- reduction in tailpipe emissions (except NO<sub>x</sub>),
- reduction in GHGs (primarily CO<sub>2</sub>), and
- improvement in lubricity of ULSD.

Biodiesel directly replaces petroleum because it is produced from renewable resources or waste fats and oil. Some estimates for the U.S. indicate that there is sufficient biomass domestically to produce 1.7 billion gallons per year - this would displace 5% of on-road diesel with biodiesel (DOE, 2008). A recent study on Low Carbon Fuel Standard for California (Farrell, Sperling et al., 2007) forecasts 1.4 billion gallons of gasoline equivalent per year for biodiesel nationwide. In the European Union, which is the largest producer and market for biodiesel, biodiesel was expected to replace around 3.5% of diesel by 2006.

Use of biodiesel improves tailpipe emissions overall with the exception of NO<sub>x</sub> which shows an increase with increasing percentage of biodiesel in the blend. The graph in Figure 10 shows the percent change for the regulated emissions for older engine models (through 1997) (EPA, 2002).

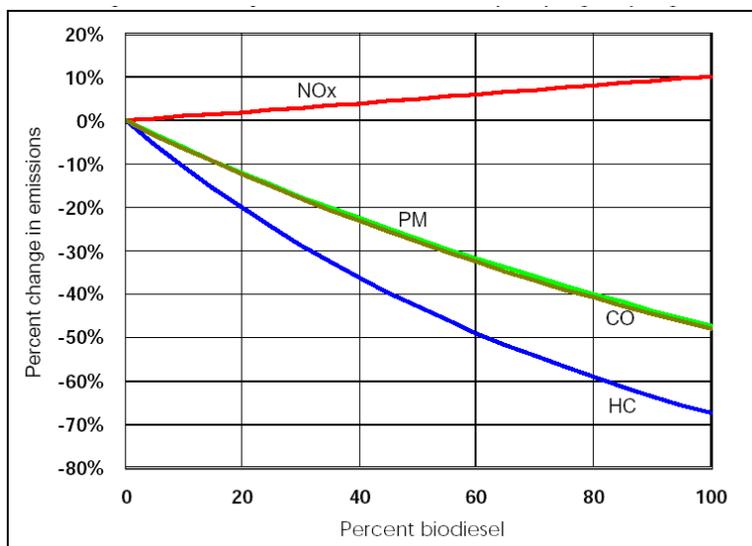


Figure 10: Effect of biodiesel on regulated emissions from engine models through 1997 (EPA, 2002).

The decrease in particulate matter (PM), carbon monoxide (CO), and hydrocarbons (HC) is significant even with lower blends of biodiesel. This is a clear advantage of using biodiesel – improved air quality in terms of three criteria pollutants. However, the emissions of NO<sub>x</sub>, the fourth criteria pollutant, increase by a few percent for B20 and up to 10% for B100 as shown on Figure 8. These results are from a study conducted on older engine models, but a later study using newer models (2004 compliant engines) confirmed the observed NO<sub>x</sub> emissions increase (McCormick, 2005). While it is not completely known why biodiesel produces higher NO<sub>x</sub> emissions, several reasons have been suggested such as higher concentration of saturated fatty acids (McCormick et al. 2001) and the different compressibility of biodiesel blends compared to diesel (Szybist et al. 2005). NO<sub>x</sub> emissions continue to be a significant disadvantage of using biodiesel especially in regions with serious smog problems.

Another expected benefit of biofuels in general, including biodiesel, is that they have the advantage over fossil fuels that they offset or reduce greenhouse gases (GHGs) and specifically carbon dioxide emissions. Use of biodiesel is expected to decrease the overall emissions of carbon monoxide when considered on a total life-cycle basis, or well-to-wheel. Reductions in GHGs on a well-to-wheels basis when using biodiesel vary from 3.8% reduction for B5, to 13% reduction for B20 (DOE, 2005; Pont et al., 2007). Several other European studies report that biodiesel can reduce GHG on a well-to-wheel basis by 38-57% (see Shippl et al. 2007 and references within). The wide and different ranges reported are caused by different methodologies and assumptions of the models. We note here that more recent research points out that the total emissions of GHGs from biofuels may be much larger if GHG emissions associated with land use effects are included and accounted for. Land use effects will be discussed in greater detail in Section 9 of this paper.

## Renewable diesel

Properties of renewable diesel are similar to fuel properties of conventional diesel. In comparison to biodiesel it is more stable and can be mixed in any proportions without affecting the vehicle technology. This gives it some advantage over biodiesel.

Since renewable diesel is a somewhat newer product, data on criteria emissions and GHG benefits are scarce. Preliminary testing done by Conoco-Philips indicates that 20% renewable diesel blends from soy oil showed reductions in NO<sub>x</sub> emission about 8% lower, CO about 60% lower, non-methane hydrocarbons 50% lower, and a slight increase in PM emissions compared to diesel fuel (Renewable Diesel Subcommittee of WSDA, 2007). Summary of results done by Neste Oil testing its NExBTL diesel fuel showed that relative to European diesel, blends of 20% renewable diesel in light-duty vehicles showed an average decrease in CO of 15% and in hydrocarbons of 20% (Renewable Diesel Subcommittee of WSDA, 2007). There was, however, no significant difference in PM or NO<sub>x</sub> emissions. Testing on heavy-duty vehicles by Scania (Fernandes, 2007) indicates an 18% decrease in NO<sub>x</sub>, 40% in benzene (considered volatile organic compounds or VOCs) and 27% in small particle emissions<sup>5</sup>.

In summary, these data indicate that in terms of criteria emissions, renewable diesel shows a significant decrease in terms HC (20-60%), small decrease in NO<sub>x</sub> emissions (8-18%), decrease in CO emissions (15-60%) and no significant decrease in PM emissions. In terms of criteria emissions, renewable diesel compared to biodiesel seems to show a similar decrease with one notable difference - no increase of NO<sub>x</sub> emissions. If confirmed by independent testing this would be an advantage of renewable diesel.

Data in terms of GHGs benefits for renewable diesel indicated that GHG reduction on the order of 20% can be achieved on the total lifecycle fuel analysis (Pont et al, 2007). For comparison, the same study finds a GHG reduction of 10-13% for biodiesel showing no benefit of one vs. the other in terms of GHG reduction potential.

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<sup>5</sup> The distinction between small particle emissions and large particle emission as related to overall PM is not clear from these results.

### ***Biodiesel ( via Transesterification)***

#### *Advantages*

- *Blends easily with diesel up to 20% content*
- *Reductions in tailpipe emissions (except NO<sub>x</sub>)*
- *Reduction in GHGs (primarily CO<sub>2</sub>)*

#### *Challenges*

- *Poor performance at lower temperatures*
- *Higher concentrations may negatively effect fuel line components*
- *Increased NO<sub>x</sub> emissions of concern*
- *GHG emissions due to land use impacts in question*

### ***Renewable Diesel (via Hydrotreating)***

#### *Advantages*

- *Similar or identical to diesel fuel*
- *Blends in any proportion with diesel fuel*
- *Decrease in criteria emissions (except PM)*

#### *Challenges*

- *No improvements in PM emissions*
- *Effects on GHG not well known*

## **6. Synthetic Fuels – Fisher-Tropsch Liquids and Dimethyl ether**

The term *synthetic fuels* refers to fuels derived via synthesis gas or syngas, a mixture of mainly H<sub>2</sub> and CO. Any hydrocarbon-containing material can be used as a feedstock for syngas; traditionally natural gas and coal have been used but more recently biomass has been introduced. When biomass is used the resulting syngas is called bio-syngas. Syngas is the intermediate energy carrier for production of second generation biofuels such as cellulosic ethanol (see Section 5.3), but also Fischer-Tropsch liquids (or F-T liquids), and dimethyl ether (DME). In this section we discuss F-T liquids and DME.

The main benefits of this pathway are:

- whole plant is used to produce the fuel
- fuels with specific properties can be designed by setting reaction parameters
- fuels can be tailored for future advanced combustion systems.

### **6.1 Definition and properties of synthetic fuels and dimethyl ether**

#### **Fischer-Tropsch liquids**

Fischer-Tropsch liquids are produced as output of the Fischer-Tropsch process which uses specific catalysts to recombine syngas to the desired product, gasoline or diesel, by building polymer chains out of the basic building blocks<sup>6</sup>. Fisher Tropsch liquids are derived from a number of feedstocks such as natural gas (Gas-to-Liquid or GTL), coal (Coal-to-Liquid or CTL), and biomass (Biomass-to-Liquid or BTL). Regardless of the feedstock, the properties of F-T liquids are similar but only BTL is considered a renewable biofuel although the other F-T liquids are considered potential alternative fuels. Primarily diesel fuel is derived by F-T processes today and to some extent jet-fuel.

Fischer-Tropsch diesel is similar in properties to renewable diesel; dominantly paraffinic. The main properties of F-T diesel are:

- Sulfur-free, low aromatic,
- Higher cetane number
- Can be used in blends with diesel using the same infrastructure and engines
- Reduction in exhaust emissions, regulated and unregulated
- No problems with material compatibility

### **Dimethyl Ether (DME)**

Dimethyl ether is the simplest of all ethers ( $\text{CH}_3\text{OCH}_3$ ) colorless, nontoxic, non-corrosive, non-carcinogenic and environmentally friendly. Today it is used as an aerosol propellant in spray cans. DME is a gas at ambient conditions but can be liquefied at moderate pressures. It can be distributed and stored much like liquefied petroleum gas (LPG) is today and in fact can use many of the same distribution and storage facilities.

The main advantages of DME are:

- High cetane number,
- Lower ignition temperature, and
- Low boiling point.

A list of properties of DME compared to diesel fuel can be found in Appendix C.

## **6.2 Principal sources and production pathways**

The sources for F-T fuels are many and while gas-to-liquids and coal-to-liquids have been dominant, biomass is being pursued as a feedstock to attain a renewable pathway. Producing synthetic fuels, regardless of the feedstock, involves multiple steps as shown on the simplified schematic diagram in Figure 11. This makes this process fairly expensive and not commercially competitive with conventional diesel at this time.

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<sup>6</sup> The Fischer-Tropsch process was developed in Germany and was used for producing liquid fuels during World War II and by South Africa later by Sasol to produce gasoline and diesel from coal. It is also known as “indirect” liquefaction of coal.

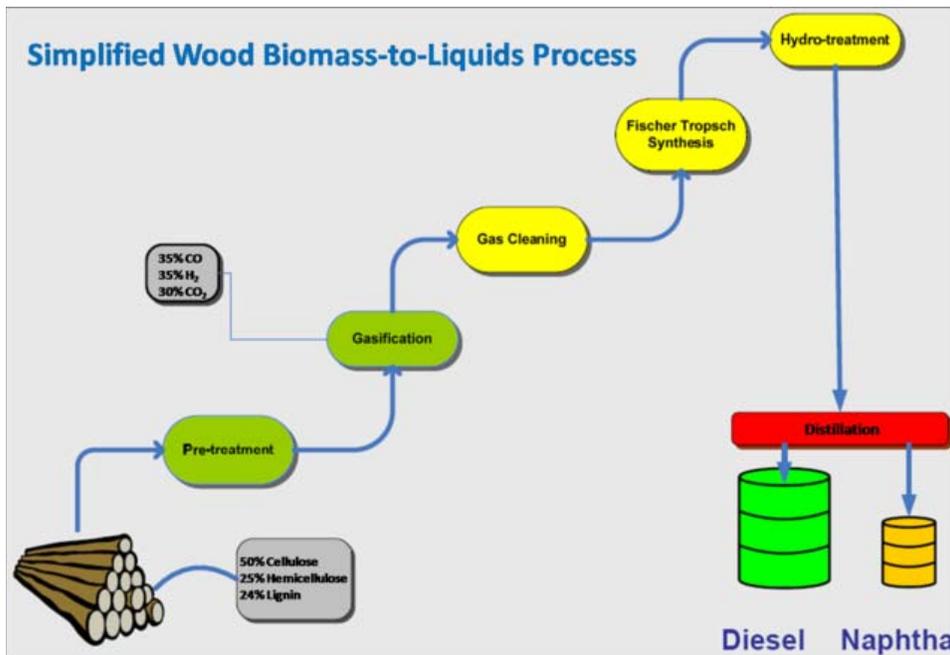


Figure 11: Simplified schematic diagram of biomass-to-liquids process (Source; Green Car Congress, 2007).

DME has traditionally been produced in a two-step process from syngas. The first step involves methanol production followed by methanol dehydration (removal of water). More recently a catalyst was developed that can make DME in one step directly from syngas. Production of DME is expensive and energy intensive and plants are economically viable only in regions where natural gas can be used as a feedstock is available at a low price.

Producing DME from biomass in dedicated biomass plants is expensive but a new production solution recently considered has higher potential for commercialization. Integrating the gasification (for syngas production) into a pulp and paper mill reduces the feedstock costs greatly. The feedstock for gasification is "black liquor." Chemrec, a Swedish company, plans to produce DME via black liquor gasification by end of 2009 in a pilot plant. Volvo is also interested in funding a BioDME project to test the overall viability of the entire chain process from raw black liquor to DME fuel for the engine and is deploying over a dozen DME trucks in Europe to test the performance of DME as an alternative fuel.

### 6.3 Uses in transportation for synthetic fuels and dimethyl ether

Fischer-Tropsch fuels can be used straight or can be blended with conventional diesel in any proportion without engine modifications. The main advantages of synthetic fuels in general are that they can be designed for the combustion system. The zero or negligible sulfur content and low aromatics eliminate many of the tailpipe emission problems. The

F-T liquids are clean-burning fuels with substantial emission benefits compared to diesel fuels.

Figure 12 shows the summarized emission reduction potential of synthetic fuels based on trials and demonstrations in Europe and estimates of those reductions in optimized engines (Alliance for Synthetic Fuel in Europe, 2007). Compared to diesel fuel, the reductions in NOx range from 5-45%, in PM from 25-40%, hydrocarbons 45-60% and CO 40-85%. The lower number represents reductions in current diesel engines and the higher number is the potential that can be achieved with engines optimized for synthetic fuels.

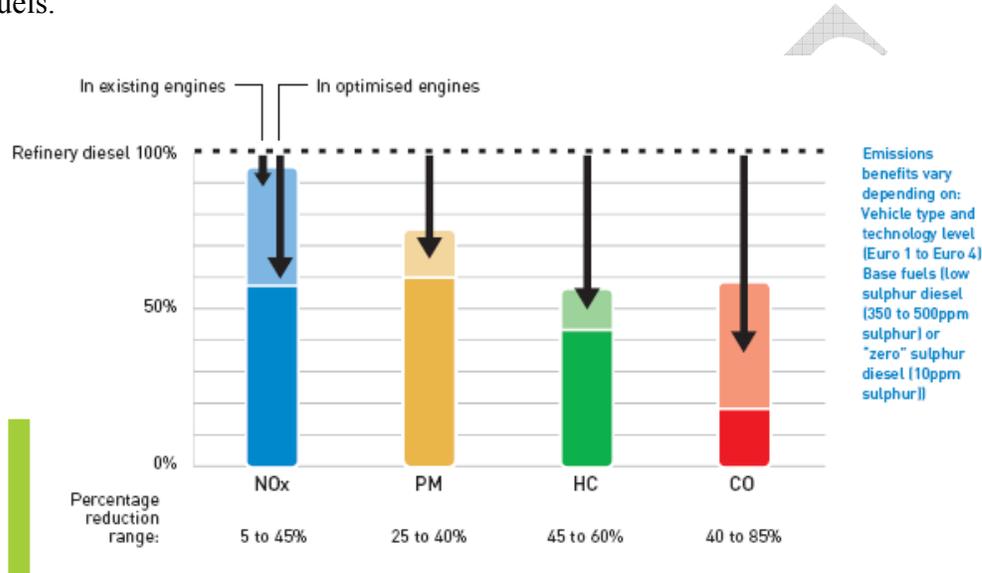


Figure 12: Emission reduction potential of F-T fuels in current diesel engines and optimized engines (Source: Alliance for Synthetic Fuels in Europe, 2007).

Environmental benefits of synthetic fuels measured on a well-to-wheel basis in terms of reduction of greenhouse gases (CO<sub>2</sub> equivalent) are shown in Figure 13.

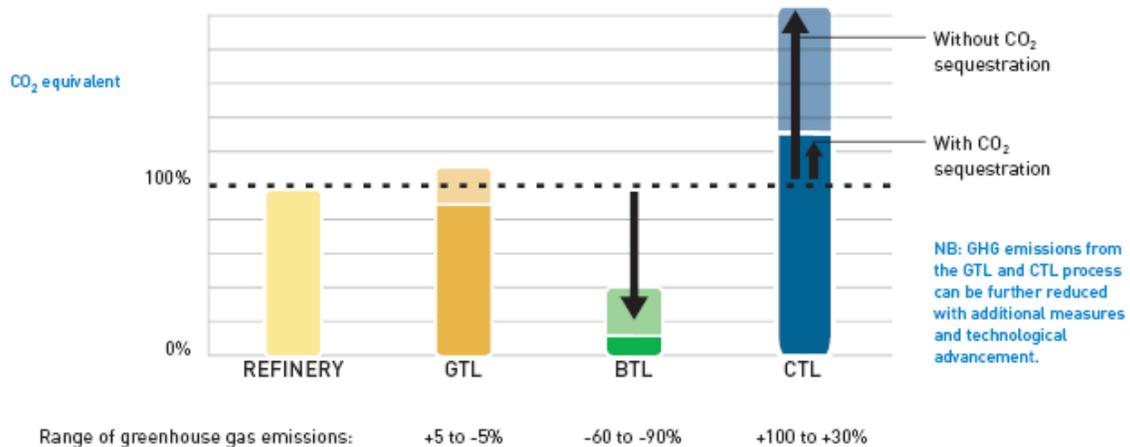


Figure 13: Change in greenhouse gases on a well-to-wheel basis of synthetic fuels (Source: Alliance for Synthetic Fuels in Europe, 2007).

It is clear that only BTL provides greenhouse benefits, ranging from 60-90%, while CTL and especially GTL show a marked increase in greenhouse gases. This is a significant drawback of coal-derived and gas-derived synthetic liquids. Another alternative would be to use biogas instead of natural gas to derive GTL liquids. This pathway may have greater overall greenhouse benefits. We did not find data specific to this process but the potential reduction in greenhouse emissions might be even lower than the values shown in Figure 15 for BTL.

DME has good combustion characteristics. The most important advantage is that it produces no soot or particulates and has NO<sub>x</sub> emissions that approach ultra-lower emission levels (ULEV) with no aftertreatment. This is a very important point because diesel engines are plagued with a tradeoff between reducing NO<sub>x</sub> or particulates. Using DME offers a way of avoiding this tradeoff - by having near zero particulates from the fuel, engine operation can be optimized to address the NO<sub>x</sub> emissions. The tailpipe CO<sub>2</sub> emissions are also lower for DME compared to diesel due to the different composition of the fuel – 67 vs 74 kg CO<sub>2</sub>/MJ (Brusstar et al., 2007).

The well-to-wheels GHG reduction for DME produced from biomass resources is even greater. A well-to-wheel analysis of future fuels in Europe (Concawe-JRC-Eurocar, 2007) compared benefits of the DME derived by two biomass pathways: from wood and wood via black liquor. The total W-T-W GHG reductions compared to diesel are 96% for DME derived from wood and 92% for DME derived from wood via the black liquor route. This later pathway is considered most favorable in terms of GHG reductions as well as being least energy intensive.

While the combustion characteristics of DME are good, the challenges are related to its physical properties such as low viscosity and lubricity which causes leakage in fuel injectors and pumps and premature wear or failure of these systems. To overcome these problems, a vehicle using DME requires a modified fuel delivery and injection system. The fuel system needs to be under pressure to maintain DME in a liquid state. The fuel tank itself needs to be larger (roughly two times) to compensate for the lower heating value. Volvo has implemented a modified fueling system for its trucks and is pursuing DME as a very favorable future alternative fuel option. Volvo has completed two generations of DME trucks and are currently field testing a fleet of fourteen DME trucks in Europe.

### ***Fischer-Tropsch Liquids***

#### *Advantages*

- *Blends in any proportion with conventional diesel fuel – can be used alone or in blends*
- *Burns clean with reduction in tailpipe emissions (regulated and unregulated)*
- *No material compatibility with fuel system*
- *Variety of feedstocks can be used – the entire plant*

#### *Challenges*

- *Process is energy intensive and expensive*
- *GHG emission benefits only from biomass feedstock*

### ***Dimethyl ether***

#### *Advantages*

- *Total elimination of PM emissions*
- *Decrease in other tailpipe emissions*
- *Reduction in tailpipe CO<sub>2</sub> emissions*

#### *Challenges*

- *Requires vehicle fuel system modifications*
- *Requires a separate distribution system*

## **7. Biogas and biomethane**

This paper focuses largely on liquid biofuels as alternatives to gasoline and diesel used because these are most widely used. There are, however, a number of vehicles, especially transit vehicles, which use natural gas as a cleaner alternative fuel. In place of natural gas, these vehicles can be powered by biogas or more accurately biomethane, derived from biomass. Biogas is a gaseous renewable biofuel that can be generated from a variety of organic waste products. Its derivative, biomethane which is cleaned up biogas, is compositionally identical to natural gas. In this section we discuss the potential of using biomethane as a transportation fuel.

### **7.1 Definition and properties of biogas and biomethane**

Biogas naturally occurs as a decomposition product of organic waste and includes landfill gas, digester gas from wastewater treatment, and biogas from decomposition of animal, food processing waste, or forest or crop residues. Biogas is composed primarily of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) with smaller amounts of hydrogen sulfide (H<sub>2</sub>S), water vapor, oxygen, and trace amounts of other hydrocarbons. The energy content (heating value) of biogas is determined by the methane content – the higher the methane content, the higher the energy content of the raw biogas. Since the methane content of biogas is relatively low, 55-70% by volume, the average heating value is 600

Btu per standard cubic foot. This is about half of the energy content of natural gas which has over 80-95% methane and a heating value over 1,000 Btu per standard cubic foot.

Biogas must be upgraded to vehicle fuel quality before it can be used as a transportation fuel. This is done by removing the non-methane components found in biogas, primarily carbon dioxide but also hydrogen sulfide and any trace elements that may negatively affect the fuel and engine system. The upgraded gas is called *biomethane* and, in terms of composition and properties, it is indistinguishable from natural gas and can be distributed and used in the same way. The main advantage is that it is a renewable fuel generated from waste biomass. For more details on sources for and economics of biomethane production, see two other Calstart papers (Calstart, 2005; Chen et al., 2010).

## **7.2 Principal sources and production pathways for biogas and biomethane**

As mentioned earlier, biogas and biomethane can be derived from a number of organic waste sources, such as:

- Agricultural wastes (e.g. manure)
- Crop residues
- Forest waste
- Industrial food processing waste
- Organic portion of municipal solid wastes
- Waste water

The process of converting organic waste feedstock into biomethane consists of two phases:

- 1) Anaerobic digestion to produce biogas
- 2) Biogas upgrading to produce biomethane.

The first step, biogas production, occurs in anaerobic digesters which are vessels or lagoons designed to exclude air and promote growth of bacteria that decompose the organic feedstock. The produced gas is captured and may be stored before being upgraded to biomethane. The upgrading process involves removing the non-methane components like CO<sub>2</sub>, hydrogen sulfide (H<sub>2</sub>S), and water. This increases the methane content of the gas, increases the heating value, and removes any corrosive components or elements that would damage the engine or fuel system. The final product is identical in composition to natural gas and can be injected into the natural gas pipelines or distributed through dedicated biomethane pipelines. Alternatively it can be pressured to compressed biomethane or liquefied at low temperatures to liquefied biomethane.

## **7.3 Uses in transportation for biogas and biomethane**

Fuel grade biomethane can be used as an alternative fuel for natural gas vehicles. It can be compressed, like compressed natural gas (CNG) or liquefied and used like liquefied

natural gas (LNG), depending on the design of the vehicle fuel system. Using biomethane offers the same benefits as using natural gas – a cleaner burning fuel compared to gasoline and diesel. Using CNG lowers the exhaust and the greenhouse gas emissions. The actual emissions will depend on the engine design, but a good estimate of the range of potential emissions benefits done by EPA based on the cleaner burning characteristic of natural gas compared to gasoline provides good guidelines (EPA, 2002). The potential emission benefits of CNG compared to gasoline from the EPA calculations are:

- Reduced carbon monoxide emissions 90%-97%
- Reduced carbon dioxide emissions 25%
- Reduced nitrogen oxide emissions 35%-60%
- Potentially reduced non-methane hydrocarbon emissions 50%-75%
- Fewer toxic and carcinogenic pollutants
- Little or no particulate matter
- Eliminated evaporative emissions.

Using biomethane provides additional greenhouse benefits by capturing and using the methane and carbon dioxide that would otherwise be released into the atmosphere from landfills, manure decomposition, and other sources. The amount of methane released from these sources is fairly large. For example, landfills, dairy and cattle farms in California account for over 75% of the methane emissions in the state (Bemis, 2006). As a greenhouse gas methane is highly reactive and significantly contributes to the climate change problem. Its concentrations in the atmosphere are lower than CO<sub>2</sub> but it is much more reactive than CO<sub>2</sub> - twenty one times more reactive. Thus, biomethane use has dual benefits; it is a cleaner renewable transportation fuel and diverts two GHGs (methane and CO<sub>2</sub>) from being emitted into the atmosphere.

In a recent study we evaluated the economics of biogas and biomethane production from manure (Chen, et al., 2010). While the price is highly sensitive to scale of operation, delivered cost of biomethane fall in the range of price variability of North American natural gas. Biomethane from manure can be produced at cost of \$5.9 per MMBTU compared to \$4.9 per MMBTU for conventional natural gas.

Existing natural gas vehicles can seamlessly run on biomethane and would require no modifications. If, however a larger portion of vehicles is expected to use biomethane, then significant conversions of vehicles are required to make the vehicle fleet operate on biomethane. One disadvantage of using natural gas or biomethane as a fuel is shorter vehicle range compared to gasoline or diesel. This is caused by the limits of gas storage on board the vehicle, as well as lower density of a gaseous fuel.

Sweden and the City of Göteborg have had great success in implementing use of biomethane for the transit vehicles as well as some private. Sweden is relying on biomethane as a near-terms alternative fuel for transportation. The vision for 2020 is to expand the program and use biomethane to replace 20% of all fossil fuel in transportation.

### ***Biogas and Biomethane***

#### *Advantages*

- *Reduction of tailpipe emissions compared to gasoline and diesel fuel*
- *Reduction of GHG emissions – both methane and CO<sub>2</sub>*
- *Variety of biomass waste can be used as feedstocks*

#### *Challenges*

- *Requires conversion of engines (NG engines)*
- *Distribution network not widely spread*
- *Shorter vehicle range due to lower energy density and storage limitations*

## **8. Advanced biofuels**

Advanced or third generation biofuels involve nascent methods of production using new enzymes, microorganisms, and algae to produce biofuels. Research and development of dedicated “energy crops” such as perennial grasses and fast growing trees is also underway. They differentiate themselves from first and second generation biofuels because they rely on feedstocks that are specifically grown for energy or enzymes and algae that employ a radically different process pathway. These fuels and pathways are largely in the research and development phase but offer great promise as key components of the long-term biofuels industry. Interest in the field has led to the growth of start-up companies investing resources in pursuing third generation biofuels. While this will not be a comprehensive review of all the technologies and companies, we review here several categories of advanced biofuels and pathways.

### **8.1 Algae-based biofuels**

Algae are considered a new source of biofuels, or more specifically biodiesel, as the oil found in algae is suitable for biodiesel production. The algal oil is generated as a means to store energy. Oil content in algae can range from 15-40% of dry weight of algae which is in the range of oil content in soy (20%) and rapeseed (40%). Algae use sunlight and CO<sub>2</sub> during their growth phase and produce oils when under conditions of environmental stress such as growth and nutrient-deficient conditions. Algae can have very high rates of growth, and under the right conditions, can double their weight in days. Some of the benefits of using algae as a feedstock are:

- Very high rates of growth
- Non-food source
- Can be used in conjunction with waste water treatment
- Can grow in salt water
- Can use waste CO<sub>2</sub> streams
- Can be grown on non-arable land

The overall process consists of cultivating the algae, separating the algae from the water, and finally extracting the oil from the algae. Current work is focused on identifying the particular strain of algae that thrive under particular conditions and divide and grow at desirable rates. Algae can be grown in principally two systems - closed and open. In the open system the algae grow in essentially just ponds which is relatively cheap but maintaining the ponds or keeping them clean is more challenging. Closed pond systems, on the other hand, work more like greenhouses but are expensive to construct although much easier to control and maintain.

The number of companies involved in algae biofuels has rapidly been growing. We provide a few examples here with a longer list in Appendix D.

- Shell formed a joint venture with HR Biopetroleum called Cellena to construct a demonstration plant to harvest algae it claims can double their mass several times a day, providing 15 times more oil per hectare than alternatives such as rapeseed.
- Algenol – developed a process to employ algae to produce ethanol rather than biodiesel. It produces ethanol by linking the production of sugars from algae in the presence of special enzymes and captures the ethanol vapors that the algae emit. The test facilities have yielded 6,000 gallons of ethanol per acre per year.
- LiveFuels started as a nationwide mini-Manhattan Project. The company is creating green crude that could be directly fed to refineries. Based in California, LiveFuels use open-pond algae bioreactors and have plans to commercialize the technology by 2010.

## 8.2 Synthetic biology and catalysts for biofuels

Rather than relying on the traditional fermentation or gasification processes, new techniques are being developed that employ synthetic biology, special enzymes, or catalysts to produce biofuels which are chemically similar to hydrocarbon fossil fuels. Various feedstocks can be used in the process, like sugarcane, crop residues, or algae and by applying specialty enzymes or microorganisms more efficient conversion is achieved. What principally differentiates these methods and technologies is that they skip the step of producing ethanol or biodiesel and instead produce a petroleum-like renewable biofuel. Most of the companies in this field are start-ups and largely in the research and development phase or initial pilot plant phase. A brief review of some companies using this approach is provided below and a longer list can be found in Appendix D.

- Amyris uses synthetic biology to convert sugars into high value chemicals and hydrocarbon fuels. Reprogrammed microbes are used to selectively convert sugars into hydrocarbon products such as gasoline, jet fuels, and diesel. They currently use sugarcane as a feedstock because it is currently the cheapest but could equally use algae as a starting feedstock. Amyris has partnered with a Brazilian ethanol distributor to commercialize the gasoline and diesel from

sugarcane. Amyris first applied its technology to production of an antimalaria drug which it is currently producing.

- LS9 has core competency in synthetic biology to design bioprocesses. The company employs genetically engineered bacteria to custom produce hydrocarbons and designer biofuels. Its product is called “renewable petroleum,” is compatible with the existing infrastructure, and can be used in vehicles “as is” or blended. In addition they have developed special enzymes that can convert fatty acids into hydrocarbons<sup>7</sup>.
- Virent, like Amyris and LS9, produces hydrocarbon fuels but uses a special catalyst and aqueous reforming (in water). The starting material can be any carbohydrate soluble in water. Virent’s reaction process is called BioForming and the final products are referred to as “bio-gasoline” or “bio-diesel,” indicating that they are biomass-derived.
- Solazyme, based in San Francisco, uses synthetic biology and genetic engineering to modify algal strains for better oil yields. They grow the algae in fermentation tanks without sunlight and by feeding it sugar, then derive the fuel from the algal oil produced. Solazyme’s Soladiesel product meets the ASTM standards and is compatible with diesel. The company has deals with Chevron in investigating the commercialization of its process.

### 8.3 New energy crops for biofuels

Further improvements to yields of biofuels can be made by identifying and growing energy crops, or crops that are specifically designed and grown to be converted to energy and fuels. In the US climate, switchgrass, hybrid poplars, hybrid willows, sorghum hybrids are some examples of energy crops which grow well. Another new potential energy crop is jatropha, a plant widely found in tropical and subtropical areas. A key advantage of energy crops is that they do not compete with food crops, and re-grow after each harvest without re-planting. A reliable and cheap source of energy feedstocks is important because most biofuel processes cite the cost of feedstock over 50 percent of the production cost.

- Ceres is a company that is identifying the genes of plants and identifying plants with desirable properties for energy crops. Most of the company’s work has focused on switchgrass (*miscanthus*). Ceres teams up with growers and biorefineries to match the seed to the particular climate and growing region.
- SG Biofuels is focusing on development of Jatropha plant as a source biofuel. Jatropha is non-edible shrub that contains high amounts of oil which can be used to produce biodiesel in a more sustainable way.

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<sup>7</sup> Transesterification converts fatty acids into esters so using enzymes to convert fatty acids to hydrocarbons has the potential to directly generate hydrocarbons (i.e. petroleum like fuel) from fats and oils.

### ***Advanced Biofuels***

#### *Advantages*

- *Use of non-food feedstocks*
- *Use of new pathways and processes to produce petroleum-like biofuels*
- *Can be directly integrated into existing infrastructure and vehicles*

#### *Challenges*

- *Mostly in R&D stage – not commercialized*
- *Presently higher costs compared to conventional fuels*

## **9. Evaluation and comparison of biofuels**

At the beginning of this paper we suggested that the most promising fact about biofuels is that they are expected to address the shortcomings experienced with fossil fuels in three main areas: climate change, air quality, and energy independence. In this section, we expand the three main criteria and compare different biofuels and pathways in terms of the improvements each one offers over their fossil fuel counterparts. We first explain the evaluation criteria that were chosen and then use the evaluation criteria to “rate” each biofuel and pathway and compare them side-by-side. Our goal was to understand how the different biofuels compare to each other and what improvements over fossil fuels they may provide.

### **9.1 Evaluation criteria**

Throughout this document in reviewing the different biofuels we discussed how they would apply to transportation and address the main issues related to transportation fuels. These included how use of biofuel would improve criteria emissions and GHG emissions or what vehicle modifications would be necessary. Basing our choice of criteria on the three main areas - air quality, climate change, and energy security - we added a few other that are specifically related to transportation, such as distribution of fuel and vehicle modification. In total, the following criteria were used to evaluate a range of biofuels:

1. Criteria pollutants
2. Petroleum reduction
3. Greenhouse gas impact
4. Distribution
5. Vehicle modification
6. Land use effects

Criteria pollutants – are those emission monitored and regulated due to their effect on air pollution problems. Criteria emissions include regulated emissions of carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), particulate matter (PM). Usually these are measured

only at the tailpipe but because we are interested in comparing biofuels from different feedstocks and sources, we rely on measurements that included the total life cycle of the fuels, usually referred to as well-to-wheels basis. This includes the cultivation of the feedstock, production, transportation, biofuel production, distribution of biofuel, and finally use in the vehicles. As we see from Figure 14, every step of the cycle generates emissions.

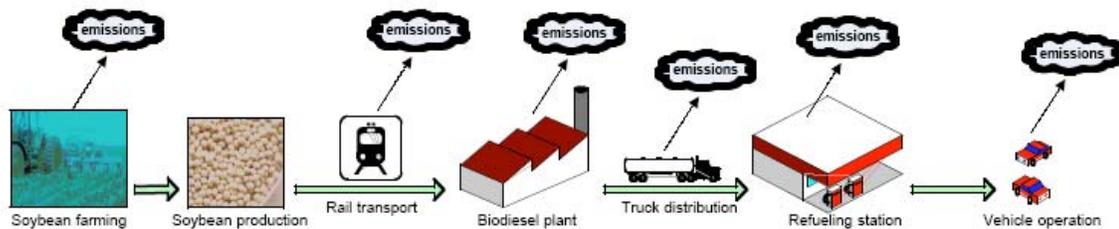


Figure 14: Lifecycle diagram of biofuel pathway and associated emissions (Delucchi, 2006).

Petroleum reduction – is a criterion that measures the ability of the biofuel to replace petroleum in transportation. This is related to availability of the biofuel and ease of introduction into the current fuel market. The numbers are based on the percentages of gasoline or diesel that can be estimated to be replaced by biofuels. This usually occurs through blending strategies, like with ethanol and biodiesel blends with gasoline or diesel. In other cases, as with DME or biomethane, it may refer to complete replacement of the fossil fuel by biofuel.

Greenhouse Gas (GHG) impacts – greenhouse gases include carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), and human-generated compounds (hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride). All of these gases have been related to climate change but primarily  $\text{CO}_2$  and  $\text{CH}_4$ , are related to use of fossil fuels in energy. It is expected that biofuels will decrease the impact of the energy use and transportation on GHG emissions overall. We therefore use this criterion to evaluate the potential impact biofuels have on GHG emissions. The GHG emissions are tracked during the entire well-to-wheel lifecycle of a biofuel.

Distribution – is an important component in evaluation of biofuels. It includes the distribution to fueling stations as well as the fueling station infrastructure. Our current distribution network is designed for liquid fuels. Introducing new fuels with new and different properties than gasoline and diesel may require modification of the current network or installation of new ones. Some biofuels may easily integrate into the existing system and would not require large modifications whereas other biofuels would require more significant modifications. This criterion evaluates the degree to which the distribution of the biofuel will be different from what is presently used for gasoline and diesel.

Vehicle modification – is the next criterion which evaluates if new adaptations and modifications on the vehicles are required to accommodate the use of biofuels. This will largely depend on the properties of the fuel. In some cases, the vehicle will require engine modification or redesign of the fueling system while in other cases the biofuel can be blended and used in conventional engines with no modifications. We consider as a standard what is currently used in diesel and gasoline vehicle designs. In the current assessment, vehicle modification is considered a short-term barrier to greater introduction of new fuels but it may be necessary in order to optimize the engine to the fuel characteristics and should not be considered a barrier or a disadvantage in the long run. In our present evaluation we use it to compare the different fuels and the ones that require fewer vehicle modifications are considered to be at an advantage.

Land use effects – is a complicated criterion but one that came into light as biofuels were being investigated. Biofuels are principally generated from biomass feedstocks that are cultivated on land and there are different types of land use effects caused cultivation. They can be divided into:

- *direct land use effects*, and
- *indirect land use effects*.

*Direct land use effects* are those directly related to growing the crops and include inputs such as land, fertilizer, energy, pesticide, water, and capital investments, and environmental effects caused by feedstock production. While these are all measurable quantities, disagreement often revolves around the size and boundaries of the system for the different inputs. For example, whether downstream effects caused by fertilizers get included or not depends often on the specific study. In summary, direct land use effects account for the inputs and outputs related to biofuel cultivation on a given area of land.

*Indirect effects*, as the name implies, are those that are indirectly caused by dedicating new land or displacing an existing crop on arable land by a biofuel crop. They are noticeable in particular in environmental effects such as destruction of natural habitats or land use change usually caused by displacement of the habitat or production of another crop on the given land. Recent studies indicate that dedicating more arable land to biofuel crops will cause a response in farming elsewhere and lead to clearing of forests or grassland for the original displaced crop land. The claiming of new land will result in a release of GHG emission from otherwise undisturbed land leading to an overall higher emissions of GHG than sequestered by the biofuel crop and displacing of fossil fuels (Fargione et al., 2008; Searchinger et al., 2008). The magnitude of the indirect effects could be larger than all the other effects combined. Indirect GHG emissions of biofuels might be larger than emission from equal amount of fossil fuels (Delluchi, 2006; Farrell, et al., 2006).

Measuring indirect effects is much more difficult and requires the use of global agricultural models. Unfortunately there is no well-accepted value for GHG emission caused by indirect land use changes and none of the life-cycle models currently in use incorporate them fully. Due to the potential magnitude of the indirect effects,

reassessment of the evaluation of biofuels is currently underway and improved frameworks are being investigated that can account for environmental, ecological and even cultural sustainability (Kammen et al., 2007).

The topic of land use impact is quite complex and new understanding is just being developed regarding indirect land use effects of different biofuels. In the absence of data for this criterion we based our rating on potentially expected impacts as implied in some of the recent studies of land use effects (Fargione et al., 2008; Searchinger et al., 2008).

## 9.2 Comparison of biofuels

To compare the different biofuels and pathways we relied on available data from the literature. Two main studies were used as sources for most of the data:

- 1) *Full fuel cycle assessment: well-to-wheels energy inputs, emissions, and water impacts by Pont et al. (2007)* which was performed for the California Energy Commission and used for the California Alternative Transportation Fuels Plan (AB 1007)
- 2) *Well-to-wheels analysis of future automotive fuels and powertrains in the European context*, performed by European Commission Joint Research Center (Concawe-JRC-Eurocar, 2007).

Both studies use the well-to-wheels approach to determine the impact of future fuel options and assess their energy use and GHG emissions. These two studies provided the source of data for three of our criteria; *criteria pollutants, petroleum reduction, and GHG impacts*. We use a scale from 1 to 5 to rate the impact of the different biofuels in comparison to the petroleum fuel baseline (either gasoline or diesel). Table C shows the rating scale for these three criteria that was used. A rating of 1 is the lowest rating reflecting a large increase in criteria pollutants, or a very small petroleum reduction, or a very small decrease in GHG impacts. The highest rating of 5 reflects a large decrease in criteria pollutant, a very large petroleum reduction potential or a very larger reduction in GHG impacts. The descriptive ratings that we assigned and the numerical values accompanying each rating are shown in Table 1. The numerical values representing percent change compared to the baseline petroleum fuel are taken from the two WTW studies mentioned above.

Table 1: Scale and rating of change in criteria pollutants, petroleum reduction, and GHG impacts of biofuels compared to petroleum baseline fuels.

<b>Rating</b>	<b>Descriptive</b>	<b>Criteria pollutants % change</b>	<b>Descriptive</b>	<b>Petroleum reduction % change</b>	<b>GHG impacts % change</b>
<b>5</b>	Large decrease	-25% and greater	Very large reduction	-(75-100%)	-(75-100%)
<b>4</b>	Small decrease	-(10-25%)	Large reduction	-(50-75%)	-(50-75%)
<b>3</b>	Same as petroleum	0-5%	Reduction	-(25-50%)	-(25-50%)
<b>2</b>	Small increase	+(5-20%)	Small reduction	-(10-25%)	-(10-25%)
<b>1</b>	Large increase	+20%	Very small reduction	-(0-10%)	-(0-10%)

The ratings for change in distribution of fuel and vehicle modifications required were assigned based on properties of the fuel in comparison to the petroleum fuels it would be replacing. The ratings scale and the description for each rating are shown in Table 2.

Table 2: Table Scale and rating of distribution of biofuels and vehicle modification

<b>Rating</b>	<b>Change in distribution of fuel</b>	<b>Vehicle modification</b>
<b>5</b>	No change - liquid	Suitable – no special adaptation
<b>4</b>	Minor change - liquid	No expensive or extensive adaptations
<b>3</b>	Major change - liquid	Expensive / extensive modifications
<b>2</b>	New distribution required - Gas in liquid form at low pressure	Complex modifications
<b>1</b>	Complex & new distribution - Gas requiring high pressure	Major modifications

There are no numerical values available that would correspond to the descriptive ratings but rather we base our ratings on the adaptations and changes that would be needed in the current distribution system of petroleum liquid fuels and vehicle design. These were individually discussed in the separate chapters dedicated to different biofuels.

Finally, we included a rating for land use effects. Very few numbers are available at this time for land use effects for the different fuels, but we considered that it was important to provide some rough guidelines on the potential land use effects. The ratings we used are divided into high (H = 5), medium (M = 3), and low (L = 1) impacts and are very preliminary. They do however provide some differentiation between biofuels that are derived from feedstocks cultivated on land (e.g. corn and soybean) and may have high land use impact versus biofuels derived from waste feedstocks (e.g. biogas and biomethane) and have low land use impact.

Table 3 shows the comparison of different biofuels and pathways using six evaluation criteria. The fuels and pathways compared come from the two life cycle studies mentioned earlier. A full spreadsheet containing the numerical values for each evaluation criterion and the corresponding score is available in Appendix E. In some cases values were not available mostly related to criteria pollutants and petroleum reduction, and we assumed a value of 3. In the case of biogas for distribution and vehicle modification we added another set of values to capture the fact that vehicles operating on natural gas do exist as we as infrastructure.

Table 3: Comparison and rating of biofuels and pathways using six criteria.

	Criteria Pollutants (W-T-W)	Petroleum Reduction	GHG Reduction (W-T-W)	Distribution	Vehicle Modification	Land Use Effects	Total
<b>Fuel &amp; Pathway</b>	<b>1-5</b>	<b>1-5</b>	<b>1-5</b>	<b>1-5</b>	<b>1-5</b>	<b>H-M-L 1-3-5</b>	<b>Max 30</b>
E-10	3	1	1	4	5	1	15
Corn E-85	2	4	1-3	3	3	1	14-16
Sugar Cane E-85	1	4	4	3	3	1	16
Cellulosic E-85	1	4	4	3	3	1	16
Biodiesel B20	4	2	2	4	5	1	18
Renewable Diesel RD30	4	3	2	5	5	1	20
Syndiesel BTL	4	3	3	5	5	3	23
Syndiesel farmed wood	-(3) <sup>b</sup>	-(3) <sup>b</sup>	5	5	5	3	24
Syndiesel from BL <sup>a</sup>	-(3) <sup>b</sup>	-(3) <sup>b</sup>	5	5	5	5	26
DME CA Poplar	5	5	5	2	2	3	22
DME Via BL	5	-(3)	5	2	2	5	22
Biogas	5	-(3)	5	1-2 (4-5) <sup>c</sup>	1-2 (4-5) <sup>c</sup>	5	20-24 26-28 <sup>c</sup>

<sup>a</sup> – BL – black liquor

<sup>b</sup> – Assumed value

<sup>c</sup> – Values assume infrastructure and vehicles for natural gas already exist

The range of total values is 14 to 28, the lowest value being for ethanol and the highest for biogas. The final rating obtained indicate that the current suite of biofuels are not optimal and that syngas and in particular biogas are preferred when evaluated on these criteria.

The biofuels evaluated fall into five main categories:

- ethanol,
- biodiesel and renewable diesel,

- synthetic fuel (syndiesel),
- DME, and
- biogas

Each biofuel is compared to its current baseline petroleum fuel. For some multiple pathways are included. The results differ within each category depending on the particular pathway which underlines the importance of not only the final biofuel product but the overall pathway.

The first overall observation is that no single biofuel rated consistently very high or consistently very low in all six evaluation criteria. Rather, each of the biofuels had some advantages and disadvantages.

Ethanol – showed an overall moderate rating of 14-16. It scores particularly poorly in terms of criteria pollutants for E10 and E85. In the case of E85 the source of the emissions is the agricultural equipment and vehicles used during cultivation of the feedstock. E85 can provide significant petroleum reduction and GHG impact reduction but requires changes in delivery and vehicle modifications. Finally, the land use impacts are rated high for the specific feedstock used in the considered pathways which compete with food crops and require large amount of land for cultivation.

Biodiesel and renewable diesel – have overall rating of 18 and 20, respectively. They rate high with respect to criteria pollutants, distribution and vehicle modification but do not offer high benefits with respect to petroleum reduction and GHG impacts. Renewable diesel rates higher overall compared to biodiesel as seen from Table 3.

Syndiesel - rated relatively high, 23-26. They easily integrate in current vehicles and can be distributed using the present distribution network used for diesel. Syndiesel offers significant improvements in criteria pollutants and moderate improvements with respect to petroleum reduction and GHG impacts. Land use effects are rated as medium to low, depending on the feedstock source (for example black liquor vs farmed wood). Based on this evaluation it seems that syndiesel biofuels are good alternatives to diesel fuel. One drawback discussed in Chapter 6 is that production of syndiesel is expensive at the moment mostly due to higher costs of the conversion process limiting wider use of syndiesel.

Dimethyl ether – has an overall rating of 22 and rated very high in terms of criteria pollutant, petroleum reduction and GHG impacts and is an excellent biofuel with respect to these criteria. However it has much lower ratings with respect to distribution and vehicle modification required for DME. Due to its properties it requires complex vehicle modifications and a distribution network similar to liquefied petroleum gas (LPG) rather than diesel. It is estimated that DME will have very low land use effects if derived from waste wood feedstock.

Biogas or biomethane – has the highest rating of 26-28. It rated very high with respect to criteria pollutants, petroleum and GHG impacts. The values for petroleum reduction

potential are not available at this point but will depend largely on regional sources for biogas feedstocks but the potential could be large and is largely untapped. Biogas is derived from waste material (agricultural waste, landfills etc.) and has very low land use effect impact. The main disadvantages of biogas are distribution and vehicle modification needed in comparison to standard liquid fuels used. If however, we take into consideration the existence of the natural gas pipelines and the availability of natural gas fueling stations as well as natural gas vehicle technology commercially available, the distribution and vehicle infrastructure ratings are higher.

## 10. Summary and recommendations

We reviewed a suite of biofuels, their feedstock sources, process pathways, and applications as transportation fuels. The main conclusions from the review are:

- Multiple feedstocks can be used to derive the same biofuel – for example multiple feedstock sources for ethanol
- Different processes can be used to derive different biofuels from the same feedstock – for example biodiesel and renewable diesel
- The feedstock and the process pathway are important to understand and evaluate the overall benefits of the biofuel
- Introducing biofuels to the current vehicle fleet offers limited benefits
- To obtain the highest efficiency benefits, biofuels need to be paired up with engines and vehicles that are optimized and modified to the properties of the biofuel
- Agricultural and land use impact are important for biofuels and should be understood
- Pathways that use waste organic matter – examples include biomethane and biogas and DME via waste wood pathway have minimal land use impacts and offer excellent strategies for reducing GHG emissions.

In an evaluation and comparison of different biofuels, we used six criteria covering criteria pollutants, petroleum reduction, greenhouse gas impact, distribution, vehicle modification and land-use effects. Using these criteria we developed a rating system with a maximum score of 30. The comparison showed that ethanol, biodiesel and renewable diesel had a moderate rating, ranging from 14-20. The next group includes syndiesel and dimethyl ether with relatively high rating ranging from 22 – 26. The highest overall rating was for biogas and biomethane (26-28). This evaluation also helps us make conclusions about the three generations of biofuels.

First generation biofuels, like ethanol and biodiesel, offer limited benefits as alternative fuels - limited displacement of petroleum and limited improvement in emissions. Greatest uncertainty is regarding GHG effects of first generation biofuels. However, we believe that their use offers important learning and should be considered a transition phase in further development and use of biofuels.

Second generation biofuels use a more diverse biomass feedstock and provide significant improvements in vehicle emissions and GHG benefits. When they use waste material as feedstocks, they provide an excellent solution in terms of GHG benefits. However, the production pathways for these fuels are generally energy intense and thus expensive, as is the example with synfuels and DME, or their use is somewhat limited currently due to the need for greater infrastructure and/or vehicle modifications (e.g. biomethane). We believe that use of synfuels and biomethane can be excellent alternative fuels and should be deployed and developed further regionally or in certain niche markets. Specifically, for regions or markets that have a high concentration of natural gas vehicles, such as transit buses, the choice of biomethane as an alternative fuel is excellent. Another niche market for biomethane is agricultural regions with high concentration of waste biomass as feedstock where the biomethane can be generated and used on-site.

Third generation or advanced biofuels are currently in research and development stage and farther from commercialization. Their attraction is that they offer to bypass or eliminate the problems listed for first and second generation biofuels by employing completely new production pathways, or use of algae or dedicated crops as feedstocks.

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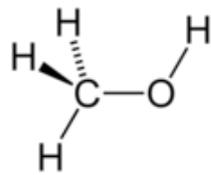
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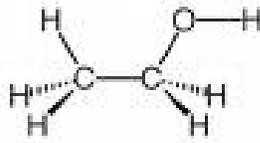
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## Appendix A - Chemical formulas and properties of alcohol fuels

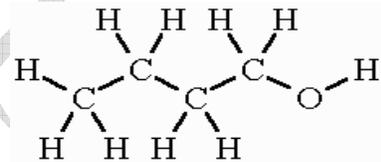
In Table A alcohols are compared to isooctane, and gasoline, for reference. Isooctane is the standard compound against which octane number is measured and by definition has an octane number of 100.



Methanol



Ethanol

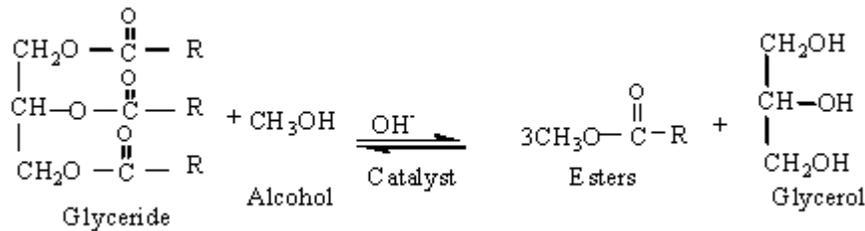


Butanol

Table A: Properties of alcohols, isooctane, and gasoline

Property	Methanol	Ethanol	Butanol	Isooctane	Gasoline
Formula	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>4</sub> H <sub>9</sub> OH	C <sub>8</sub> H <sub>18</sub>	C <sub>4</sub> -C <sub>12</sub>
Lower heating value, MJ/kg	15.74	21.16		30.65	31.4 - 33.0
Volumetric energy content, MJ/liter	15.7	21.2	29.3	30.6	31.6
Density, kg/m <sup>3</sup>	790	790	809	690	720 - 780
Water solubility, wt% water in fuel	100	100		negligible	negligible
Research Octane Number (RON)	106	109	96	100	95

## Appendix B - Properties of Biodiesel and Renewable Diesel



Transesterification reaction producing biodiesel

Table B: Properties of biodiesel and renewable diesel

Property	Diesel	Biodiesel <sup>a</sup>	20% Renewable Diesel <sup>b</sup>	NExBTL Diesel <sup>c</sup>
Lower heating value, BTU/gal	~129,050	~118,170	-	129,156
Viscosity, @ 40°C	1.3-4.1	4.0 - 6.0	2.4	2.9 to 3.5
Lubricity, microns	300-600	<300	597	-
Cetane Number	40-55 <sup>d</sup>	48-65	51.2	84 - 99
Sulfur, ppm	<15	0	8	<10
Cloud Point, °C	-15 to 5	-3 to 12	-10	5 to -30
Pour Point, °C	-15 to -15	-15 to 10	-14	

a - Source: U.S. DOE, 2006

b - Source: Renewable Diesel Subcommittee of WSDA, 2007

c - Source: Neste Oil presentation, CEC March 9, 2006

d - National average cetane number for diesel is 42-44

## Appendix C - Properties of DME

Table C: Properties of dimethyl ether and diesel.

<b>Property</b>	<b>DME</b>	<b>Diesel</b>
Boiling point °C.	-24.9	180-360
Heating Value, MJ/kg	28.8	42.5
Liquid density at 20 °C, kg/m <sup>3</sup>	668	840-890
Vapor pressure at 20 °C , bar	5.1	-
Cetane Number	55-60	40-55
Autoignition temperature, °C	235	200-300

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## Appendix D -List of Biofuel Companies

<b><i>Alcohol Fuels</i></b>		
<b>Abengoa Bioenergy Biomass of Kansas, LLC</b>	<a href="http://www.abengoabioenergy.com">www.abengoabioenergy.com</a>	Owns and operates several biomass to bioethanol plants in the US and is focused on production of cellulosic ethanol. It is also the largest European producer of bioethanol. The company has received DOE funding.
<b>Adkins Energy</b> 4350 W Galena Road, P.O. Box 227 Lena, Illinois 61048	<a href="http://www.adkinsenergy.com">www.adkinsenergy.com</a>	A 69 million dollar corn-to-ethanol facility with a cogeneration plant which processes approximately 15 million bushels of corn annually.
<b>AltraBiofuels</b> 11911 San Vicente Blvd. #325 Los Angeles, CA 90049	<a href="http://www.altrabiofuels.com">www.altrabiofuels.com</a>	Develops and licenses biofuel technologies. Currently is running two plants in the US producing ethanol from corn with a third in development to produce ethanol from other feedstocks.
<b>Aventine Renewable Energy</b> 120 North Parkway PO Box 1800 Pekin, IL 61555	<a href="http://www.aventinerei.com">www.aventinerei.com</a>	Produces ethanol from corn as well as associated bi-products.
<b>BioEnergy International, LLC</b> 99 Longwater Circle Suite 201 Norwell, MA 02061	<a href="http://www.bioenergyllc.com">www.bioenergyllc.com</a>	Specializes in development of novel biocatalysts for production of high value specialty chemicals and renewable fuels from sugars.
<b>BlueFire Ethanol</b> 31 Musick Irvine, CA 92618	<a href="http://www.bluefireethanol.com">www.bluefireethanol.com</a>	Conversion of cellulosic waste materials to ethanol using concentrated hydrolysis processes.
<b>Butamax Advanced Biofuels LLC.</b> Experimental St. Building 268 200 Powder Mill Rd. Wilmington, DE 19880	<a href="http://www.butamax.com">www.butamax.com</a>	Joint venture between BP and DuPont for production of butanol. The main focus of the new company will be to develop a technology program to produce biobutanol from many different types of feedstocks.
<b>Cilion</b> P.O. Box 819 Goshen, CA 93227	<a href="http://www.cilion.com">www.cilion.com</a>	Producer and distributor of low cost, environmentally sustainable biofuels. Cilion's ethanol plants are strategically located near large population and livestock market areas.
<b>Cobalt Technologies</b> 500 Clyde Avenue Mountain View, CA 94043	<a href="http://www.cobalttech.com">www.cobalttech.com</a>	Production of biobutanol using microbial strains optimized for converting plant material.
<b>Coskata</b> 575 Weaver Parkway, Suite 100 Warrenville, IL 60555	<a href="http://www.coskata.com">www.coskata.com</a>	The process can produce ethanol from a wide variety of feedstock by gasification followed by conversion of ethanol from syngas using microorganisms and bioreactors.

<b>Gevo</b> 345 Inverness Drive South, Building C, Englewood, CO 80112	<a href="http://www.gevo.com">www.gevo.com</a>	Use of biocatalysis and host organisms to convert biomass to butanol and isobutanol.
<b>Iogen Corp.</b> 310 Hunt Club Rd. East, Ottawa, Ontario, Canada	<a href="http://www.iogen.ca">www.iogen.ca</a>	Iogen is focusing on developing and commercializing enzymes used in hydrolysis of biomass for cellulosic ethanol processes.
<b>Lignol</b> Unit 101 - 4705 Wayburne Drive Burnaby, BC Canada	<a href="http://www.lignol.ca">www.lignol.ca</a>	Development of fuel-grade ethanol and other biochemical co-products from cellulosic biomass feedstocks. Its solvent based pre-treatment technology is used for wood-pulp applications; conversion of cellulose to ethanol; and the production of biochemical co-products.
<b>Mascoma</b> 61 First Street Second Floor East Cambridge, MA 02142	<a href="http://www.mascoma.com">www.mascoma.com</a>	Mascoma's research laboratories are now developing a new generation of enzymes, microbes and processes for economical conversion of cellulosic feedstocks into ethanol in a one-step process.
<b>Pacific Ethanol</b> 400 Capitol Mall, Suite 2060, Sacramento, CA 95814	<a href="http://www.pacificethanol.net">www.pacificethanol.net</a>	Production and marketing of ethanol derived from a variety of sources. Special focus for plants is in Western United States.
<b>Poet</b> 4615 North Lewis Avenue Sioux Falls, SD 57104	<a href="http://www.poet.com">www.poet.com</a>	Poet uses a dry mill process to convert feedstocks into ethanol. The process employs special enzymes allowing more direct conversion of sugars into ethanol.
<b>Range Fuels</b> 11101 W. 120th Avenue, Suite 200 Broomfield, CO 80021	<a href="http://www.rangefuels.com">www.rangefuels.com</a>	Two step thermo-chemical process to produce ethanol and methanol. First step produces syngas and the second step converts it to biofuel.
<b>Verenium Corp.</b> 55 Cambridge Parkway, 8th Fl. Cambridge, MA 02142	<a href="http://www.verenium.com">www.verenium.com</a>	Developing enzymes to ferment and convert cellulose and hemicellulose to ethanol. Verenium operates a pilot plant for production of cellulosic ethanol.
<b><i>Biodiesel / Renewable Diesel</i></b>		
<b>Biodiesel Industries</b> 435½ El Sueno Rd. Santa Barbara, CA 93110	<a href="http://www.pipeline.to/biodiesel">www.pipeline.to/biodiesel</a> 805/683-8103	Produces and develops biodiesel production facilities in the U.S.
<b>Biotane Fuels</b> 86-600 Avenue 54 Coachella, CA 92236	<a href="http://www.biotanefuels.com">www.biotanefuels.com</a>	Production of biodiesel via esterification of vegetable or animal fat.

<b>Blue Sky Bio-fuels</b> 200 Park Blvd. PMB 286, Oakland, CA 94602	<a href="http://www.blueskybio-fuels.com">www.blueskybio-fuels.com</a>	Recycling of waste cooking grease into biofuel (esterification).
<b>Greenline Industries</b> 24 Tiburon St. San Rafael, CA 94901	<a href="http://www.greenlineindustries.com">www.greenlineindustries.com</a> 866/247-4763	Develops, fabricates and produces groundbreaking technology in biodiesel production equipment employing waterless technology.
<b>Imperium Renewables</b> 1741 First Avenue S Third Floor Seattle, WA 98134		Production of biodiesel
<b>Kreido Biofuels</b> 1070 Flynn Road Camarillo, CA 93012	<a href="http://www.kreido.com">www.kreido.com</a>	Developing biodiesel production plants with technology that greatly reduces the time of reaction and increases conversion yields.
<b>Neste Oil</b> Keilaranta 21, Espoo Finland	<a href="http://www.nesteoil.com">www.nesteoil.com</a>	Production of renewable diesel (green diesel) made from renewable raw materials. The product is more similar to petroleum diesel and can directly replace it.
<b>Primafuel</b> One World Trade Center-8th Floor, Long Beach, CA	<a href="http://www.primafuel.com">www.primafuel.com</a>	Advanced technology solutions for production of biodiesel as well as ethanol. Primafuel develops infrastructure and technology for biofuels.
<b>Propel Fuels</b> 808 R Street Suite 101 Sacramento, CA 95811	<a href="http://www.propelfuels.com">www.propelfuels.com</a>	Propel builds, owns and operates a growing network of clean fueling points
<b><i>Algae-based Biofuels</i></b>		
<b>Algenol</b> 28100 Bonita Grande Drive, Suite 200 Bonita Springs, FL 34135	<a href="http://www.algenolbiofuels.com">www.algenolbiofuels.com</a>	Algenol has advanced 3rd generation biofuels technology producing ethanol from algae through a process powered by the sun.
<b>Aquaflow Bionomics</b> P O Box 3295 Richmond Nelson 7050 New Zealand	<a href="http://www.aquaflowgroup.com">www.aquaflowgroup.com</a>	Economically producing biofuel from wild algae harvested from open-air environments. It sources its algae from algae-infested polluted water systems, cleaning the polluted environment in the process.
<b>Aurora Biofuels</b> 1301 Harbor Bay Parkway Alameda, CA 94502	<a href="http://www.aurorabiofuels.com">www.aurorabiofuels.com</a>	Aurora utilizes microalgae to generate bio-oil, which can be converted into biodiesel. Developed at the University of California at Berkeley, the company is using genetically modified algae to efficiently create biodiesel.

<b>Bionavitas, Inc.</b> 8469 154th Avenue NE Redmond, WA 98052	<a href="http://www.bionavitas.com">www.bionavitas.com</a>	Developing high volume production growth of micro-algae for production of biodiesel.
<b>HR BioPetroleum</b> 7597 Eads Ave., Suite A La Jolla, CA 92037	<a href="http://www.hrbp.com">www.hrbp.com</a>	The core technology is a photosynthetic production system that economically grows proprietary algae strains at a commercial-scale. HR BioPetroleum is partnering with other companies to produce biofuels from algae.(joint venture Cellana).
<b>Inventure Chemical</b> P.O. Box 530 Gig Harbor, WA 98335-0530	<a href="http://www.inventurechem.com">www.inventurechem.com</a>	A startup that engineers/selects algae species for their growth properties and suitability for the processing of in-demand functional chemicals, and fuels.
<b>Live Fuels, Inc.</b> 1300 Industrial Road, Suite 16 San Carlos CA 94070	<a href="http://www.livefuels.com">www.livefuels.com</a>	Instead of attempting to convert algae directly into ethanol or biodiesel, this startup is trying to create green crude that could be fed directly through the nation's current refinery system. The Menlo Park, Calif-based startup uses open-pond algae bioreactors.
<b>OriginOil</b> 5645 West Adams Los Angeles, CA 90016	<a href="http://www.originoil.com">www.originoil.com</a>	OriginOil's industrial process, with its patent pending devices and methods, optimizes this environment to help algae cells grow at their natural maximum rate - achieving a doubling of the algae population in as little as a few hours.
<b>Sapphire Energy</b> San Diego, CA	<a href="http://www.sapphireenergy.com">www.sapphireenergy.com</a>	Developing industrial algae strains through synthetic biology and breeding techniques. These processes result in a product called Green Crude which can be refined into the fuels we use every day – gasoline, diesel and jet fuel
<b>Solazyme</b> 225 Gateway Blvd. South San Francisco, CA 94080	<a href="http://www.solazyme.com">www.solazyme.com</a>	Solazyme uses an indirect photosynthesis bioproduction process using microalgae to produce algal oil which can be converted to fuel and other biochemicals.
<b>Solix Biofuels</b> 430B N. College Ave. Fort Collins, CO 80524	<a href="http://www.solixbiofuels.com">www.solixbiofuels.com</a>	Solix process will permit large scale commercialization of biocrude extraction from algae. The biocrude is converted to biodiesel and green diesel.
<b><i>Advanced Biofuels - Synthetic Biology and Genomics</i></b>		
<b>Amyris Biotechnologies</b> 5980 Horton St., Suite 450 Emeryville, CA 94608	<a href="http://www.amyrisbiotech.com">www.amyrisbiotech.com</a>	Leveraging breakthroughs in synthetic biology to provide a consistent, cost-effective supply of biofuels and other high-value natural compounds. Currently developing a biofuel (1) gasoline substitute that contains more energy than ethanol and is fully compatible with today's cars and the existing petroleum infrastructure; and (2) diesel substitute that can achieve lower costs and much greater scale than vegetable oil based biodiesels.
<b>Ceres</b> 1535 Rancho Conejo Blvd. Thousand Oaks, CA	<a href="http://www.ceres-inc.com">www.ceres-inc.com</a>	Plant biotechnology company utilizing cutting-edge genomics technologies to deliver sustainable solutions in energy production (specifically, ethanol derived from cellulosic biomass) and other areas.

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<b>Codexis</b> 200 Penobscot Drive Redwood City, CA 94063	<a href="http://www.codexis.com">www.codexis.com</a>	Codexis produces biocatalysts such as enzymes and fermentation strains for chemical processes and is working with Shell to develop next generation biofuels from non-food sources.
<b>Genencor</b> 925 Page Mill Rd. Palo Alto, CA 94304	<a href="http://www.genencor.com">www.genencor.com</a>	Research and development of enzymes including enzymes for production of cellulosic ethanol fuel from agricultural and forestry byproducts. In 2000, Genencor was awarded a grant from the U.S. Department of Energy to develop low-cost cellulases and other enzymes for the production of ethanol from biomass.
<b>Iogen</b>	<a href="http://www.iogen.ca">www.iogen.ca</a>	See under ethanol /alcohol fuels.
<b>LS9</b> 1300 Industrial Rd., Suite 16 San Carlos, CA 94070	<a href="http://www.ls9.com">www.ls9.com</a>	Biotechnology company pursuing industrial applications of synthetic biology to produce proprietary biofuels designed to closely resemble petroleum derived fuels, but be renewable, clean, domestically produced and cost competitive.
<b>Mascoma</b>	<a href="http://www.mascoma.com">www.mascoma.com</a>	See under ethanol/alcohol fuels
<b>Novozymes</b> Krogshoejvej 36 2880 Bagsvaerd Denmark	<a href="http://www.novozymes.com">www.novozymes.com</a>	Using modern gene technology Novoenzymes isolates specific enzymes for a variety of conversion processes including biofuels.
<b>Qteros</b> 100 Campus Drive 6th Floor Marlborough, MA 01752	<a href="http://www.qteros.com">www.qteros.com</a>	Uses a unique type of microbe to convert biomass into ethanol in one step, potentially replacing a multistep process that uses expensive enzymes to break down cellulose.
<b>Verenium Corp.</b>	<a href="http://www.verenium.com">www.verenium.com</a>	See under ethanol/alcohol fuels.
<b>Other</b>		
<b>Bioenergy Solutions</b> 200 New Stine Rd., Suite 220 Bakersfield, CA 93309	<a href="http://www.bioensol.com">www.bioensol.com</a>	Provides the infrastructure necessary to create renewable natural gas from animal waste, then shares the revenues from the sale of gas and carbon credits with the farmer or food processor.
<b>GRT, Inc</b> 861 Ward Drive Santa Barbara, CA 93111	<a href="http://www.grt-inc.com">www.grt-inc.com</a>	GRT is commercializing a new process of converting natural gas and flare gas into higher value liquid fuels and chemicals.
<b>Syntroleum</b> 5416 S. Yale Ave. Suite 400 Tulsa, OK 74135	<a href="http://www.syntroleum.com">www.syntroleum.com</a>	The Syntroleum Processes convert fats, biomass, natural gas, coal, and other carbon bearing feedstocks into ultra-clean fuels. It is based on the Fischer-Tropsch and Bio-refining technologies.
<b>Virent Energy Systems</b> 3571 Anderson St. Madison , WI 53704	<a href="http://www.virent.com">www.virent.com</a>	The process uses aqueous reforming and catalysts to convert any sugars soluble in water into biogasoline molecules. Plant derived sugars are converted to premium bio-derived gasoline, jet fuel and diesel.

## Appendix E - Comparison of biofuels and pathways using six evaluation criteria

Fuel	Criteria Pollutants Change (WTW)				Score	Petroleum Reductio	Score	GHG Impact	Score	WTW GHG	from end table	Score	Distribution	Score	Vehicle Modification		Land Use		
	VOC	CO	NOx	PM											Score	Score			
					1-5	2012	1-5	CEC Analysis, WTW		JRC/CONCAWE based on g CO2eq/km				1-5		Score			
<b>Ethanol</b>	E-10	-1%	0%	-2%	0%	3	-3%	1	-1%	1				4		5	H		
	Corn E-85	2%	0%	8%	1%	2	-(70 to 73%)	4	-36% CA corn; -15 to 28% Midwest; +15% coal plant	1-3				3		3	H		
	Sugar Cane E-85	2 to 5%	0%	32 to 45%	10 to 17%	1	-(73 to 75%)	4	-68%	4.0				3		3	H		
	Cellulosic E-85	2 to 5%	0%	32 to 45%	10 to 17%	1	-(73 to 75%)	4	-(60 to 72%)	4.0				3		3	H		
	Cellulosic wood or straw E-100										-(75 to 91%)		4				H		
	Sugar cane or wheat E-100										-30%	-(30 to 80%)	3-5			3	H		
<b>Methanol (F-C)</b>																			
<b>Butanol (advanced fuel)</b>																			
<b>Biodiesel (FAME)</b>																			
	B100																		
	B20	-20%	-10%	3%	-8%	4	-(15 to 17%)	2	-(10 to 13%)	2		-(40 to 70%)	3-4			4	H		
<b>Renewable Diesel</b>																			
	RD30	-20%	-10%	3%	-8%	4	-29%	3	-20%	2						5			
	NexBTL 20%Blend															5	L		
<b>Synthetic Fuels</b>																			
	BTL30	-21%	-14%	-4%	-6%	4.5	-28%	3	-28%	3						5	M		
	Syn-diesel waste wood via BL										-94%	-96%	5			5	L		
	Syn-diesel farmed wood										-84%	-91%	5			5	M		
<b>DME</b>																			
	CA Poplar		<<<	<<<	~90%	5	-95%	5	-94%	5							3		
	Waste wood via BL		<<<	<<<	~90%	5					-94%	-96%	5			2	L		
	Farmed wood		<<<	<<<	~90%	5					-84%	-92%	5			2	3		
<b>NG Biogas</b>																			
	Dry Manure	-72%				5	-99%	5	-(20 to 30%)	39481									
	Liquid Manure						-99%	5	?(probably greater than NG)	5						1	L		
	MSW										-188%	-94%	5						
											-75%								
		5	Large Decrease	-25%		5	Very Large Reduction	75-100%	5	75-100%				5	No Change - liquid	5	Suitable - no special adaptation	L	Low impact
		4	Small Decrease	-10%		4	Large Reduction	50-75%	4	50-75%				4	Minor Change -liquid	4	No expensive or extensive adaptation		
		3	Same as petroleum	0-5%		3	Reduction	25-50%	3	25-50%				3	Major Change -liquid	3	Expensive /extensive mod	M	Medium impact
		2	Small Increase	(5-10%)+		2	Small Reduction	10-25%	2	10-25%				2	Gas in liquid at low p	2	Complex modifications		
		1	Large Increase	20%+		1	Very Small Reduction	0-10%	1	0-10%				1	Gas - high p	1	Major & extensive mods	H	High impact