Gaps in the Research of 2nd Generation Transportation Biofuels

This publication is the final report of Task 41, Project 2. It was initiated by Mr Larry Russo, Office of Biomass Program, US Department of Energy in January 2006 and led by Dr Michael Ladisch of Purdue University, USA. The participants were Finland, the Netherlands, Sweden, United Kingdom, USA, and the European Commission.

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ANALYSIS AND IDENTIFICATION OF GAPS IN RESEARCH FOR THE PRODUCTION OF SECOND-GENERATION LIQUID TRANSPORTATION BIOFUELS

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ABSTRACT

Project 2 was initiated on 13 January 2006 based on a proposal by Larry Russo (Office of Biomass Program, US Department of Energy) to the IEA Bioenergy Executive Committee. Dr Michael Ladisch (Laboratory of Renewable Resources Engineering, Purdue University) joined as the Project Co-Leader. A statement of work was then finalised and submitted for approval by the Executive Committee with a start date of June 1, 2006. The project co-leaders worked with a team of participants from Finland, the Netherlands, Sweden, UK, USA, and the European Commission to develop a global view of gaps in research for addressing production of second-generation liquid biofuels. The Project 2 team developed its findings based on inputs from participating countries through a series of conference calls, published reports, and discussion and review with experts who are carrying out work associated with related Tasks within IEA Bioenergy. Research gaps were found in cellulosic ethanol, Fischer-Tropsch liquids and green diesel, dimethyl ether and P-Series fuels.

Lignocellulosic ethanol is derived from pre-treatment, hydrolysis, and fermentation of the resulting sugars from cellulosic sources such as wood chips, agricultural residues, and grasses. Green diesel is a high boiling component, not derived from vegetable oil, obtained either from Fischer-Tropsch synthesis or through pyrolysis of biomass. Dimethyl ether has potential as a high quality fuel for diesel engines and is produced by converting syngas into methanol followed by dehydration of methanol to dimethyl ether. P-Series fuel is a mixture of ethanol, methyltetrahydrofuran, pentanes and higher alkanes, and butane. Methyltetrahydrofuran may be produced from dehydration of pentose and glucose sugars to form furfural and levulinic acid respectively, which when hydrogenated result in methyltetrahydrofuran.

Common denominators in gaps for these different fuels and the biochemical or thermochemical processes used to produce them are given by three main areas. These are:
• catalysts and biocatalysts;
• feedstock preparation and bioprocessing; and
• systems integration.

In the biocatalyst (or catalyst) area research is needed to achieve more robust, versatile, and cost-effective catalysts. The catalytic systems must be less subject to inhibition and more stable in the presence of chemically complex feedstocks derived from biomass materials. With bioprocessing, the gaps lie in economic enzyme production, reduction of enzyme inhibition, development of pentose utilising and cellulase producing micro-organisms, feedstock preparation (pre-treatment), and inhibitor removal. For thermochemical systems, the list is analogous except the term 'catalyst' replaces 'enzyme' or 'micro-organism'.

Gaps were identified in feedstock preparation, with this term being broadly defined. Feedstocks are defined as biomass materials entering the process, as well as gases derived from biomass and used for catalytic formation of diesel or other fuels. Pre-treatment of cellulosic materials so that they are more efficiently converted to fermentable sugars is one form of feedstock preparation, and research that addresses the fundamental science and process development of pre-treatments should be viewed as a research gap. Clean-up of gases derived from biomass before the gases enter a catalytic step is another important research gap. Both areas impact on the efficiency, longevity, and cost of biocatalysts and catalysts.

Systems integration and the integration of bioengineering with chemical engineering for cost-effective production and use of second-generation fuels represents a third research gap. This area encompasses gaps that must be addressed in better understanding the infrastructure required to deliver second-generation fuels and policies that would accelerate their introduction to the market place.

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Cover: Data acquisition of biomass fermentation to ethanol, NREL, Golden, USA. (Courtesy DOE/NREL and W. Gretz)

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1. INTRODUCTION

Liquid transportation fuels derived from biomass reduce the dependence on crude oil imports and therefore increase the stability of national fuel markets. Most bioenergy systems generate significantly less greenhouse gas emissions than do fossil fuels and can even be greenhouse gas neutral if efficient methods for biofuels production are developed (Tyson, 1993).

Technologies to produce the first-generation liquid fuels, such as ethanol from starch and sugar, and biodiesel from vegetable oils, are commercially installed. However, fossil fuel replacement is limited due to feedstock availability. Second-generation liquid transportation fuel utilises more abundant biomass such as agricultural and forestry residues. Technologies to convert lignocellulosic biomass into liquid fuels are available, but have not yet been applied to large-scale production (Balat, 2005).

Funds that promote the development of cellulosic ethanol conversion technologies are limited and must therefore be focused where they can have the most impact (Wyman, 2007). The same applies for the synthetic biofuels. The purpose of this study was to initiate an analysis of future steps that are needed to achieve a major increase in production of liquid transportation fuels from renewable resources, including consideration of the impact of improved reaction rates, product selectivity, and yields. Improving the process efficiency and the economics of technologies that can produce biofuels on a sustainable basis is the vehicle to reach scale-up in production.

For the sake of completeness, this publication introduces widely commercialised biofuel technologies (Section 2), as well as all currently developed second-generation liquid transportation biofuel technologies. This publication's focus however, is on those technologies that still require more R&D.

2. CURRENT BIOFUEL MARKETS

A range of biofuels is available in the market either as a substitute for fossil liquid transportation fuels or as an additive blended with conventional fuels. Biofuel markets vary among different countries, since market share and types of biofuels used depend on availability of biomass, transportation fuel infrastructure (i.e., gasoline versus diesel-powered vehicles), and national energy policies.

2.1. Bioethanol from starch and sugar

Bioethanol is ethanol derived from biological feedstocks utilising fermentation processes. This definition encompasses ethanol produced through fermentation of monosaccharides. Monosaccharides that are currently capable of being fermented to ethanol by yeast or bacteria include xylose and glucose.

Bioethanol production dominates in USA and Brazil with outputs in 2006 of 4.9 billion gallons (EIA, 2007c) and 4.7 billion gallons (EIA, 2007a), respectively; Europe consumes much less ethanol (EUBIA, 2007b). Although demand for fuel ethanol more than doubled between 2000 and 2004, ethanol satisfied only 2.9% of USA transportation-energy demand in 2005 (EIA, 2007c; Houghton et al., 2006). Over 95% of ethanol production in the USA comes from corn, with the rest made from wheat, barley, milo, cheese whey, and beverage residues (Solomon et al., 2007). The main source of ethanol in Brazil is sugarcane. Brazil accounted for almost 90% of the ethanol imported into the USA in 2005 (Solomon et al., 2007).

[1] one gallon = 3.785 litres

Table 1: Bioethanol production in the USA, Brazil, and Europe

Bioethanol	USA	Brazil	Europe
Output 2006 (billion gallons)[1]	4.9	4.7	0.42
Main sources	Corn	Sugar cane	Wheat, sugar beet
Market share	2.9%	40%	< 0.1%

Table 1 gives an overview of ethanol production in the three regions. Production has increased significantly in 2006 and 2007 as new plants have started up, adding an estimated 2 billion gallons[1] of production in the USA (RFA, 2007a).

Historical development and the abundant natural resources fostered bioethanol use in both Brazil and the USA (Solomon et al., 2007). Benefits of ethanol blended in gasoline are increased octane number, and improved emission quality (less carbon and hydrogen, more oxygen [C_2H_5OH ethanol vs. C_8H_{18} gasoline]). Ethanol is also a safe replacement for toxic octane enhancers in gasoline such as benzene, toluene, and xylene (Balat, 2005). However, at low blends (<20%) evaporative emissions may occur that need to be addressed by appropriate technical means (Poulopoulos et al., 2001).

Bioethanol from starch and sugar is produced when natural yeast ferments 6-carbon sugars. In commercial ethanol production, sugar can be obtained directly from sugarcane (Brazil), sugar beet (Europe), or hydrolysis of starch-based grains such as corn (USA) and wheat (Europe). In the latter, the starch feedstock first needs to be ground to a meal which is further hydrolysed to glucose by means of enzymes. The mash is fermented using natural yeast and bacteria. Finally, the fermented mash is separated into ethanol and residues (for feed production) via distillation and dehydration. The process scheme for ethanol production from starch is shown in Figure 1.

Bioethanol derived from starch and sugars is not considered to be part of the gap analysis for this publication since the science and technology of this biofuel are already developed and commercialised.

Another source of sugar is lignocellulosic (woody) biomass which must be hydrolysed in order to release fermentable sugars from the crystalline cellulose structure (Wyman, 1994) (see Section 3.1).
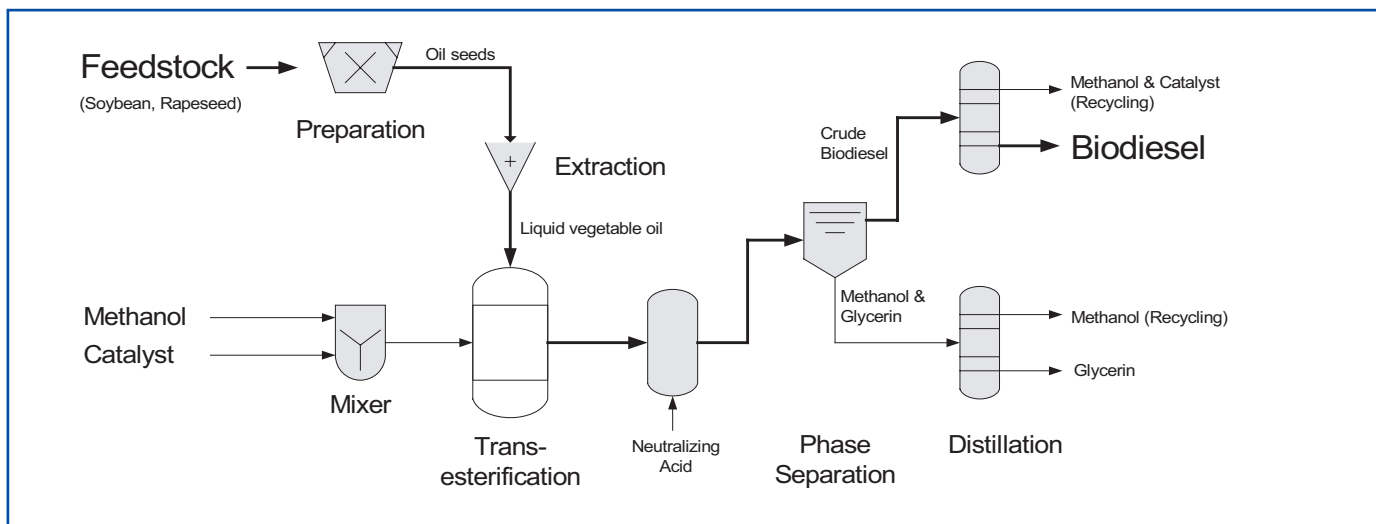
2.2. Renewable diesel-type fuels from vegetable oils and animal fats

There are currently two major pathways to produce a biofuel similar to diesel fuel using vegetable oils and animal fats as feedstocks: transesterification and hydrogenation.
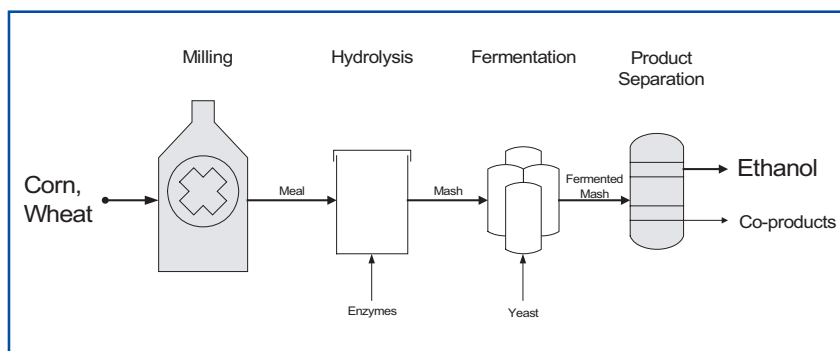
Figure 1: Process flow diagram for ethanol production from starch.

Figure 2: Process flow diagram for biodiesel production.

It is also possible to produce a fuel similar to diesel from lignocellulosic biomass. This involves producing synthesis gas with subsequent treatment via the Fischer-Tropsch process, or by making pyrolysis oils and then further treating these via petrochemical processes to form diesel analogues. Collectively, these processes are often referred to as Biomass-to-Liquid processes (BTL) which are described in detail in Section 3.

Biodiesel is a triglyceride derived from transesterification of vegetable oil with methanol or ethanol using either an acid or base catalyst.

Biodiesel from vegetable oil can be used directly as a fuel with minor engine modifications or blended up to 20% into petroleum derived diesel fuel without modifications in areas of the world where climate conditions permit the use of such a fuel. Biodiesel is more commonly used in Europe. However, few of the diesel car manufacturers give guarantees for 100% biodiesel, and for instance in cold climates as in Scandinavia, unblended biodiesel cannot be used in winter time.

Biodiesel consumption was approximately 1.2 billion gallons[2] in 2006 (= 3,852,000 tons/year). Rapeseed (84%) and sunflower (13%) were the main feedstock (European Commission, 2007). Recently, significant quantities of palm oil have been imported in the European Union (EU) for biodiesel production due to the relatively low cost of palm oil. Biodiesel consumption in the USA was 75 million gallons[1] in 2005 (Guzman, 2007) and 263 million gallons[1] in 2006 (Lichts, 2007), mainly in heavy duty engines. Total diesel fuel consumption in 2006 was 63 billion gallons[1] (EIA, 2005). Blended in conventional diesel fuel, the most important biodiesel source in the USA is soybean (Guzman, 2007). Table 2 compares the biodiesel consumption in the USA and Europe.

Table 2: Biodiesel consumption in the USA and Europe

Biodiesel	USA	Europe
Consumption 2006 (billion gallons)[1]	0.263	1.2
Main sources	Soybean	Rapeseed

Triglycerides are a major component of vegetable oils and animal fats. Biodiesel is produced when triglycerides are transesterified with alcohols into alkyl esters (Huber et al., 2006). Transesterification transforms the large branched molecule structure of the oils into smaller, straight chained molecules similar to the standard diesel hydrocarbons (EUBIA, 2007a).

Figure 2 illustrates the conversion of an oil-containing feedstock into biodiesel. Prior to transesterification, the seed from which the oil is extracted must be cleaned, dried, and hulled. The oil can then be extracted by pressing or through solvent extraction (Erickson et al., 1980). The triglycerides in the extracted oil are transesterified in a reactor with methanol and a base catalyst. Methanol and the base form an alkoxide which then reacts with the triglycerides to produce an intermediate, which then decomposes into the desired alkyl ester (biodiesel) (Schuchardt et al., 1998). In the following steps, the products from the reactor, biodiesel and glycerin, are neutralised, and the crude biodiesel phase can easily be separated from the glycerin phase due to their large difference in density. After separation, the excess alcohol is removed from both the biodiesel and the glycerin via flash evaporation or distillation. The methanol is then recycled to the beginning of the process, and the glycerin can be further purified and sold as a by-product for other industrial purposes (NBB, 2007).

The EU has chosen to focus on biodiesel production because of the superior fuel economy of diesel engines, the agricultural practices in Europe, and the fact that many cars run on diesel fuel in the EU (Huber et al., 2006). Biodiesel reduces most serious air pollutants (particulates, CO, hydrocarbons, air toxics) and the additional oxygen in biodiesel enables a more complete combustion. However, NO_x emissions are higher compared to conventional diesel (Monyem and Van Gerpen, 2001).

Shell recently announced a joint venture with Hawaiian-based HR BioPetroleum to produce biodiesel from algae (Shell and HRBP, 2008) Algae refer to a variety of microbes with photosynthetic activity. The investigated species convert sunlight, carbon dioxide, and nitrogen into triglycerides, carbohydrates, and lignin. Using algae as a source of triglycerides for biodiesel production has the advantage of very high yields per hectare. According to HR BioPetroleum, cultivation of algae yields up to 15 times more oil per hectare than terrestrial crops such as rape, palm, and soya, which is the result of a two-year continuous commercial algae production. Furthermore, seawater and coastal land are used for cultivation and these are unsuitable for conventional agriculture (HRBP, 2008).

Algae production has been studied in both closed photobioreactors and open ponds. A photobioreactor can produce algae continuously, but oil concentration is low and production cost is high. Algae production in open ponds results in initially very high growth rates with high oil contents. However, algae growth is limited due to contamination of the desired culture by other organisms (Sheehan et al., 1998).

A description of current commercialised algae cultivation is outlined by Huntley and Redalje (2007). Production takes place in a combined

[2] 3,852,000 ton/year = 161,787,000 GJ/year (1 ton = 42 GJ); Energy content of Biodiesel (LHV) = 0.034 GJ/litre; 3.785 litres = 1 gallon

system of a closed photobioreactor and an open pond. First, microbes are grown at constant conditions (i.e., temperature, pH) that favour continuous cell division and prevent contamination. On a daily basis, the culture is transferred from the photobioreactor to an open pond where it is exposed to greater environmental stress (i.e., nutrient deprivation). While this stimulates oil production and increases cell concentration, the short residence time in the open pond prevents contamination. Current oil production costs were estimated to be US$84 per barrel. A reduction to US$50 per barrel is claimed to be possible if improvement in the technology is achieved (Huntley and Redalje, 2007). The goal is to produce triglycerides in areas that are otherwise unsuitable for agriculture. Triglycerides derived from algae can be transformed using conventional biodiesel production methods.

Hydrogenation-derived renewable diesel (HDRD) is produced by refining animal fats or vegetable oils in an oil refinery. This typically involves hydrogenation of triglycerides using existing refinery infrastructure. Neste Oil (Finland) and ConocoPhillips (USA, Ireland) currently produce HDRD commercially using proprietary processing technologies (US DOE, 2007a). Neste Oil uses its NExBTL process to produce HDRD. Most NExBTL fuel properties are similar to conventional diesel while the cetane number is increased. Furthermore, NExBTL fuel is more stable than biodiesel and can be blended in conventional diesel in all ratios without implications for vehicle technology (Neste Oil, 2007). The main difference between Neste Oil and ConocoPhillips is that the former utilises a direct process (the oils are hydrogenated in dedicated plants) while the latter employs an indirect process (the oils are added in a petroleum oil refinery downstream).

While renewable diesel production technologies have been developed in large-scale facilities in the past, continuing efforts are needed to improve processes for biodiesel production (such as utilisation of glycerol and other by-products in order to improve economics and greenhouse gas balances) and to increase production of hydrogenation-derived renewable diesel (i.e., NExBTL). However, renewable diesel is not considered to be part of the gap analysis for this publication since biodiesel production is a mature technology, and HDRD production is currently being commercialised.

2.3. Biomethane

Methane (CH_4) can be used as a transportation fuel if it is compressed to a liquid at pressures of about 20 MPa. There are two main sources of methane: natural gas, which consists of at least 90% methane, and biogas (Balat, 2005). Biogas, derived from anaerobic decay of organic material, consists mainly of 55-75% of methane and 30-45% of CO_2. It can be produced naturally from decay under water or in the guts of animals, and artificially in airtight digesters (Hilkiah et al., 2007). For industrial applications, the simplest type of biogas digester is a batch vessel consisting of a closed container such as a drum, tan, or pit in the ground into which the digestible material is loaded (Steadman, 1975). Anaerobic digestion is used worldwide for the treatment of industrial, agricultural, and municipal waste-water and sludge, as well as for treatment of municipal solid wastes (Kiely, 1998). Biogas is widely used for heating purposes and/or electricity generation, and may be upgraded by the separation of CO_2, resulting in biomethane which usually has a higher methane concentration than natural gas. In some countries (e.g., Finland, Sweden and France), a few city-buses or vehicles owned by farmers are powered by biomethane (Hilkiah et al., 2007). A benefit of biomethane combustion is that it produces low amounts of greenhouse gases due to the relatively low portion of carbon in the gas (Balat, 2005).

Although further development work is needed to reduce the costs of CH_4-CO_2 separation unit operations, biomethane is not considered to be part of the gap analysis for this publication since the science and technology of this biofuel are already developed and commercialised.

2.4. Biofuels as blends in conventional transportation fuels

The use of biofuels as blends in conventional transportation fuels optimises the burning characteristics inside the combustion chamber by increasing the octane number or the cetane number, for gasoline or diesel fuels, respectively. Increasing octane or cetane provides more complete combustion, and enables a higher compression ratio. Higher octane increases the fuel's resistance to auto-ignite, which is desirable in spark-ignition internal combustion engines. The opposite is sought for diesel engines, where higher cetane provides more time for completing the combustion process. The cetane number represents the time delay between fuel injection and ignition. In both cases, a more complete combustion reduces air pollution from exhaust emissions, and the higher compression ratio increases the theoretical thermal efficiency of the combustion engine.

For more than 20 years, methyl tert-butyl ether (MTBE) and bioethanol have been used as gasoline additives in the USA, mainly because of their benefits as oxygenates to increase octane (RFA, 1997). Recently however, bioethanol has been replacing MTBE due to environmental concerns (Nadim et al., 2001). Bioethanol as a gasoline additive prevents icing of the fuel and is compatible with current engine technologies (RFA, 2007c). Flexible Fuel Vehicles (FFVs) can be powered with E85 which is a fuel containing 85% bioethanol and 15% gasoline. FFVs are cars with slightly modified engines including a fuel sensor that detects the ethanol/gasoline ratio, and optimised materials (i.e., for the tank and fuel lines) to tolerate the alcohol (RFA, 2007b).

So far, bioethanol has been blended in gasoline at low ratios. Bioethanol has the potential to replace a large portion of gasoline consumption, assuming that car manufacturers will continue providing the market with more ethanol-compatible vehicles. This makes it worthwhile to compare their characteristics as fuels in combustion engines. A selection of important chemical properties of gasoline and ethanol are summarised in Table 3.

Table 3: Chemical properties of gasoline and ethanol

Chemical properties	Gasoline	Ethanol
Density (kg/m³) [1]	725	790
Lower Heating Value (MJ/L) [1]	35	23.4
Octane [2]	87	115
Oxygen content (% per weight) [2]	0	35

[1] ORNL, 2007; [2] EIA, 2007b.

A comparison of ethanol and gasoline is complex due to the variety of factors it has to take into account (such as driving conditions, season, or the state of tune of the vehicle). Nevertheless, some important facts can be mentioned. A study at the University of Michigan, Dearborn, investigated the effects of different ethanol and gasoline blends on exhaust emissions, energy utilisation and combustion characteristics (Clark et al., 2004). The results show that hydrocarbon and nitrogen oxide emissions are lower for ethanol, whereas carbon monoxide emissions are similar. These environmental benefits are derived from the oxygen content in the ethanol. The higher density and the lower energy content (lower heating value) of the ethanol means that a given volume will weigh more and also be consumed more quickly to achieve a given energy input to the engine compared with gasoline. However, the higher octane number allows the engine to have a higher compression ratio which increases the theoretical thermal efficiency of the combustion. Therefore, an engine will theoretically consume a higher volume of ethanol compared with gasoline, but this can be counterbalanced in modern engine technologies by a more efficient combustion. The results in this study are based on testing of a single engine without modifications for ethanol use. Some sources state that an FFV using E85 experiences only 10-15% drop in fuel economy (NEVC, 2007). FFVs are designed to be fuelled with an ethanol/gasoline blend.

However, FFVs are not optimised to E85. Therefore, it has to be mentioned that there is improvement potential if engines are optimised for ethanol use in the future.

In the EU, preference is given to blending ethyl-tertio-butyl-ether (ETBE) into gasoline, rather than bioethanol. ETBE has characteristics similar to those of bioethanol (i.e., increased octane). It is produced by combining bioethanol and isobutylene derived from petroleum refining (Enguidanos et al., 2002). ETBE is widely used in France and Spain, the leading countries in ethanol application

Biodiesel has beneficial characteristics for the environment and good lubricating properties. However, Iowa State University estimates that if all of the vegetable oil and animal fat were used to produce biodiesel, only 15% of on-highway diesel fuel in the USA could be replaced with biodiesel (Gerpen, 2007). This implies that biodiesel use as a replacement for petroleum diesel is very limited in the USA. Current oilseed production can be increased, but this will result in land use competition with food production. As mentioned earlier, the role of biodiesel as a blend in conventional transportation fuels is therefore not further investigated in this publication.

Figure 3: Pre-treatment effect on lignocellulosic material. (From Hsu et al., 1980).

3. CURRENT RESEARCH AND CHALLENGES IN SECOND-GENERATION BIOFUELS

The majority of the currently produced biofuels are based on edible feedstocks. Large-scale replacement of fossil transportation fuels is therefore a very unlikely scenario. However, the science and technologies of first-generation technologies are well known. This knowledge as well as the existing production facilities can be beneficial in developing more promising biofuel technologies.

3.1. Bioethanol from lignocellulose

Lignocellulosic material (woody biomass) is characterised by its strength and complexity due to a network formed from hemicellulose and cellulose in close association with lignin. A number of processing steps are required to overcome this complex structure to make it accessible to hydrolysis
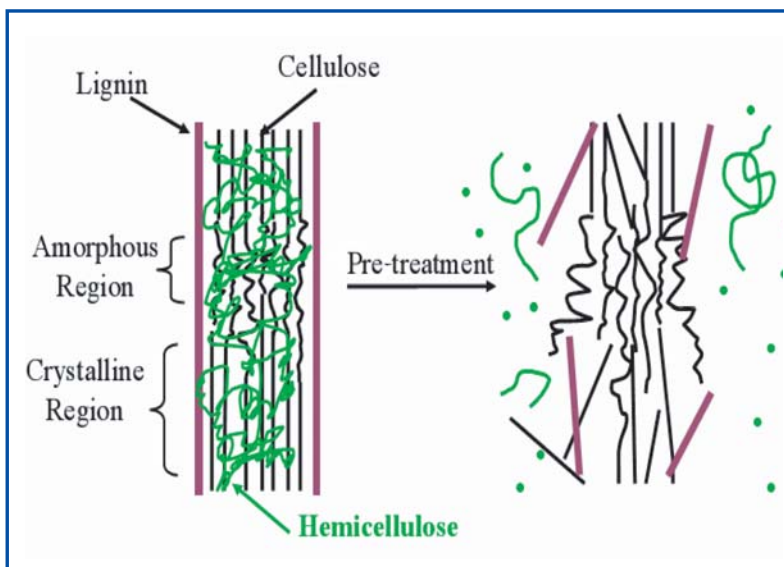

Dr Mike Himmel, NREL, explaining the use of imaging and the research pathways for elucidating structure and function of cellulosic materials in relation to their resistance to hydrolysis. Courtesy L. Russo, USDOE.

and fermentation. The first step in producing cellulosic ethanol is biomass handling where the size of the lignocellulose is reduced to make handling easier and ethanol production more efficient. During pre-treatment, the cellulose structure is disrupted, the lignin seal is broken, and the hemicellulose is partially removed. This increases the surface area that is accessible to enzymes. Pre-treatment is one of the many steps in the cellulose-to-ethanol process, but represents a currently critical step for hydrolysis. An effective pre-treatment is performed at conditions that avoid degradation of pentose from hemicellulose, or glucose from cellulose, and limit formation of degradation products that inhibit growth of fermentative micro-organisms (needed for ethanol production). Pre-treatments should also limit energy, chemical, and/or enzyme usage in order to limit the cost of the pre-treatment process itself (Mosier et al., 2005). The effect of pre-treatment on the structure of lignocellulose is depicted in Figure 3.

After pre-treatment, the cellulose and hemicellulose chains are more accessible to enzymes in the forms of polymers and oligomers. Hydrolysis by enzymes breaks the chains into monomers. Enzymatic hydrolysis has the potential to make ethanol, derived from cellulose biomass, competitive compared to other liquid fuels on a large-scale (Wyman, 1999). The monomers are fermented by wild-type yeast or by genetically engineered bacteria or yeast that ferment both glucose and xylose. Saccharomoyces are natural yeasts which feed on the glucose to produce ethanol and are currently applied in large-scale corn-to-ethanol or sugarcane-to-ethanol industries. However, ethanol production from lignocellulose requires not only fermentation of glucose, but also fermentation of pentose sugars. Saccharomoyces are not able to ferment pentose. One way to manage fermentation of pentose is the utilisation of genetically modified yeasts, specifically engineered for this purpose (Ho et al., 2000). The result of fermentation is a mixture of water, ethanol, and residues, with CO_2 being formed and removed as a gas from the fermentation.

Hydrolysis performed separately from fermentation is known as separate hydrolysis and fermentation (SHF). Cellulose hydrolysis carried out in the presence of the fermentative organism is referred to as simultaneous saccharification and fermentation (SSF). Simultaneous saccharification of both cellulose (to glucose) and hemicellulose (to pentose) and co-fermentation of both glucose and pentose (SSCF) is realised by genetically engineered microbes (Mosier et al., 2005). Ethanol is recovered from the fermentation broth by distillation (Ladisch et al., 1984). The residual lignin, unreacted cellulose and hemicellulose, ash, enzyme, organisms, and other components end up in the bottom of the distillation column. These materials may be concentrated, and burned as fuel to power the process, or converted to various co-products (Wyman, 1994). Furthermore, expensive catalysts are recovered for re-use. CO_2 is recycled into plant matter through production agriculture or forestry.
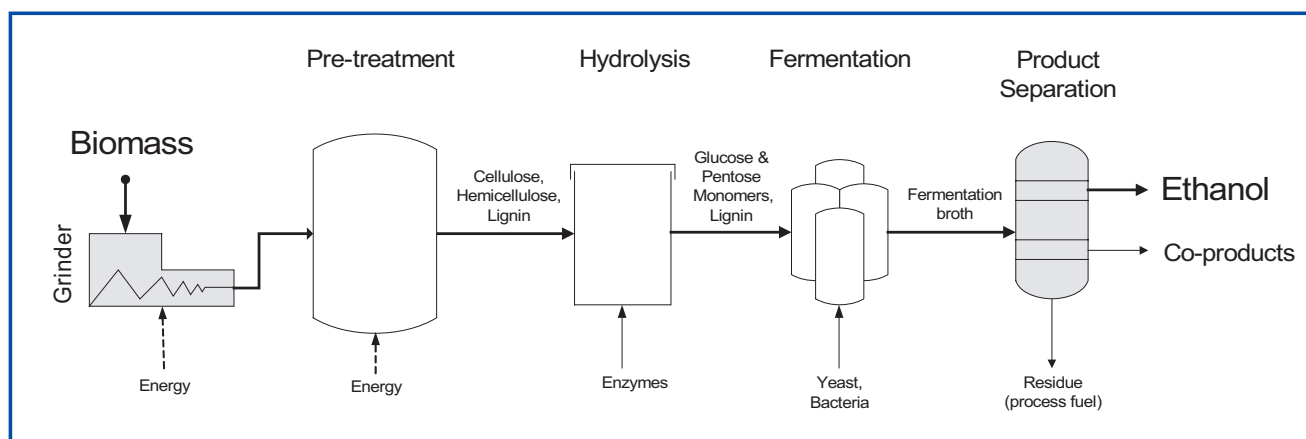
Figure 4: Process flow diagram for ethanol production from lignocellulose.

Figure 4 shows the process sequence for ethanol production from lignocellulose. The key steps are preparation (size reduction) of biomass, pre-treatment to soften up the structure of the cellulose, hydrolysis to break the cellulose down into sugars, and then fermentation of the sugars to ethanol. Product separation is the final step and consists of distillation followed by drying using either a molecular sieve or a corn-based adsorbent.

Cellulosic ethanol production is not yet commercially installed and large-scale production of cellulosic ethanol has not been proven to be economically feasible, although significant potential exists. According to Wyman et al. (2005), biological conversion 'has the potential to achieve nearly theoretical yields'. Research on cellulosic ethanol production has been carried out mainly at laboratory scale. Pilot plants may exist, even though no work has been published yet. According to Houghton (2006), lignocellulose as a renewable source of liquid transportation fuels is 'abundant domestically and globally' and 'can be used readily by current-generation vehicles and distributed through the existing transportation-fuel infrastructure.' Recent technological improvements have considerably reduced the cost of enzymes and the cost of pre-treating biomass (Houghton et al., 2006; Wyman et al., 2005). In addition, new approaches, such as the genetic modification of the biomass' lignin structure (Chapple, et al., 2007; Chen and Dixon, 2007), have the potential to reduce the need for pre-treatment. However, high capital costs coupled with the high cost of capital increase the risk of a first of a kind technology and therefore hinders commercialisation (Wyman, 2007; Wooley et al., 1999).

Dr Rick Elander, NREL, describing methods for screening hydrolysis potential for biomass materials. Courtesy L. Russo, USDOE.

3.2. P-Series fuel

P-Series fuel is a mixture of ethanol, methyltetrahydrofuran (MTHF), pentanes and higher alkanes, and butane. It is defined as an 'alternative fuel' by the US Department of Energy. Pure Energy Corporation holds the exclusive worldwide licence to manufacture and distribute the P-Series fuels (US DOE, 1999).

MTHF has an octane number of 87, which is the same as regular gasoline, and contains 20% oxygen by weight, thus helping to improve emission quality (Huber et al., 2006). The formulas for P-Series fuels can be adjusted for warm and cold weather as well as for different market demands. Depending on the composition, P-Series fuels are derived 60 to 100% from non-petroleum sources, on an energy basis. Pure Energy Corporation has represented that both MTHF and ethanol will be produced from lignocellulosic feedstocks such as waste paper, agricultural waste, and urban/industrial waste. Evaluations of life-cycle greenhouse gas emissions by both Pure Energy Corporation and the US Department of Energy show that P-Series fuels will reduce CO_2 emissions by 50% compared to reformulated gasoline (US DOE, 1999).

MTHF can be produced via dehydration of pentose and glucose sugars towards furfural and levulinic acid, respectively. However, MTHF production can also become part of the processing in the modern biorefinery in order to achieve higher thermal and economic efficiencies than those of separate processes. In a biorefinery, bioethanol production is associated with the production of a variety of other chemicals, including furfural and levulinic acid which can serve as feedstocks to produce MTHF (Huber et al., 2006). A research gap is in the integration of this type of system within a biorefinery to make best use of both types of technologies: bioprocessing and catalytic conversion of sugars.

Furfural is a degradation product of the acid hydrolysis of xylan or other pentosan from either pre-treated or untreated lignocellulose. During hydrolysis, a small portion of the pentose sugars from hemicellulose is degraded to furfural which can easily be separated from the pentose fraction (Antal et al., 1991). Furfural can further be hydrogenated to MTHF (Ahmed, 2005; Huber et al., 2006). Levulinic acid is produced when glucose monomers degrade during acid hydrolysis of cellulose. After separation from the glucose fraction via distillation, levulinic acid can be used for production of MTHF. Bozell et al. (2000) describe the hydrogenation process of levulinic acid to form MTHF.

The benefit of levulinic acid as a base chemical for production of P-Series fuels has been outlined. Nevertheless, levulinic acid can also be converted into levulinic esters through an esterification process in the presence of alcohol and a catalyst (Manzer, 2006). Octane number and oxygen content ranges of levulinic esters are similar to those of ethanol, making them ideal for gasoline additives. Levulinic esters can also be used as oxygenates for diesel fuels (Huber et al., 2006).

3.3. Synthetic bio Fischer-Tropsch diesel

Fischer-Tropsch (FT) processes form long chain hydrocarbons from catalytic combination of CO and H_2. If the gaseous components are derived from biomass instead of coal, the resulting product is referred to as being 'bio'. The basic steps of synthetic bio FT diesel production are pre-treatment, gasification, gas cleaning and conditioning, FT synthesis, up-grading, and recycling, as described by Hamelinck et al. (2004). Pre-treatment includes drying and size reduction of the biomass. The required energy for drying can be extracted from within the plant, i.e., FT process heat. The pre-treated biomass is gasified by means of either pure oxygen or steam. Gasification using air would result in a producer gas which contains mainly CO and H_2, but also CO_2, CH_4, and large amounts of N_2. Air-blown gasifiers are therefore used almost only for power generation with less demanding gas quality requirements (Boerrigter and Uil, 2002). Gasification with oxygen is more expensive, but the biosyngas which is formed has a better quality due to the lower concentration of nitrogen. Throughout the following process description, the term syngas is used, but both producer gas and the biosyngas can serve as a feed gas for the consequent processing steps.

Biomass can be gasified by means of different reactors depending on a variety of factors, i.e., the desired syngas quality. The produced syngas contains impurities (volatiles, organic compounds, and inorganic compounds) which must be removed. The syngas is cleaned of volatiles and inorganic compounds using well known technologies from fossil FT diesel production (Boerrigter and Uil, 2002). Organic compounds, referred to as tars, are higher molecular weight hydrocarbons that develop during gasification of biomass. Tars in the product gas are problematic because they condense in exit pipes and on particulate filters leading to blockages and clogged filters. They also cause clogging of fuel lines and injectors in internal combustion engines (Huber et al., 2006). There are currently three basic pathways to overcome the tar-related problems:
- fluidised-bed gasification + catalytic reforming
- fluidised-bed gasification + solvent-based tar removal
- entrained-flow gasification at high temperatures.

Cracking the tars into smaller hydrocarbons is considered to be an option for gas conditioning (Hamelinck et al., 2004). Research is ongoing to develop catalytic tar removal technologies that apply elemental iron (Nordgreen et al., 2006) or nickel-based catalysts (Pfeifer and Hofbauer, 2007). Currently, a demonstration plant for gasification of wood chips with subsequent catalytic cracking and FT synthesis is being built in Finland in a joint venture of the Technical Research Centre of Finland (VTT), Neste Oil, and Stora Enso (Neste Oil and Stora Enso, 2007). A process flow diagram for syngas production using catalytic cracking is depicted in Figure 5.

Solvent-based tar removal has been realised in the OLGA (oil-based gas washer) technology which aims at the elimination of tar-related problems (Boerrigter et al., 2005). In contrast to catalytic cracking, this approach does not focus on the tar content, but on the behaviour of tar. In the OLGA, the liquid tars are collected in a scrubbing liquid after the product gas is cooled with oil. Subsequently, entrained fines and oil droplets are removed electrostatically. Gaseous tars are absorbed in a separate scrubbing column. While the collected tars are recycled to the gasifier, the remaining organic compounds in the product gas will not cause downstream problems as the dew-point of the gas is well below 20°C. Three test facilities for the OLGA tar removal technology have been installed including a demonstration plant in Moissannes, France, in 2006 (Zwart, 2007).

Tar formation can be avoided when syngas is produced via entrained-flow gasification at high temperatures. This technology requires sub-millimetre-sized feedstock particles. Reducing the biomass to this size is difficult and expensive, particularly for woody biomass. However, the biomass can be pre-treated in order to improve its size reduction behaviour. Torrefaction is a thermochemical pre-treatment process at a temperature level of 200-300°C in the absence of oxygen (Bergman et al., 2005). Torrefaction can improve the milling characteristics of the biomass and also have a positive impact on transport and storage due to the hydrophobic nature of torrefied biomass.

Another approach to produce a tar-free syngas was made in Freiberg, Germany. Choren Industries GmbH has built a 45 MW$_{th}$ pilot plant where the biomass is gasified in two successive reactors. First, a low-temperature gasifier breaks down the shredded biomass into volatiles and solid char. The tar-rich gas then passes through an entrained-flow gasifier where it is reacted with oxygen. Since the combustion performs at very high temperatures, the ash melts and flows outside the combustion chamber, resulting in a tar-free gas (NNFCC, 2007b).

In FT synthesis (see Figure 6) one mole of CO reacts with two moles of H_2 on a catalyst surface, thus producing long-chained hydrocarbons and water ($C_nH_{2n}+2 + n\ H_2O$). Iron-based catalysts, such as cobalt (Co) or iron (Fe), are used mainly for FT synthesis. According to Martinez and Lopez (2005), applying a ZSM-5 catalyst coupled with a Co or Fe catalyst shifts the product distribution to a higher level of C_{10-20}. This process merges the syngas into a range of products, depending on the applied catalyst and the reaction parameters. The C_{10+} fraction is hydro-cracked into the desired diesel fuel (C_{10-20}) while the smaller fraction (C_{1-4}) is reconverted into syngas. The C_{5-9} fraction is a high-quality chemical which can be sold to serve as an intermediate for other products. Recycling this fraction would result in higher green diesel yields, but the recycling step is economically not attractive (Boerrigter and Uil, 2002). In the last step, the diesel fuel is up-graded to meet market requirements. Fuel production can also be combined with generating electricity which reduces the output of FT liquids, but improves the overall efficiency and decreases the investment costs (no recycling of FT off-gas) (Boerrigter and Uil, 2002).
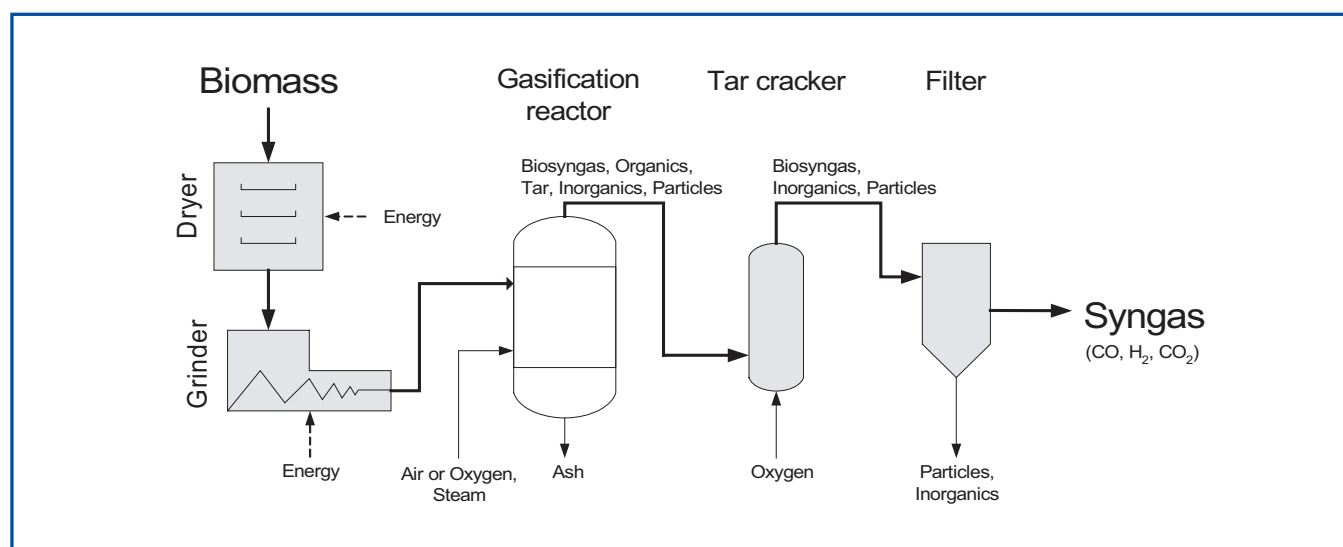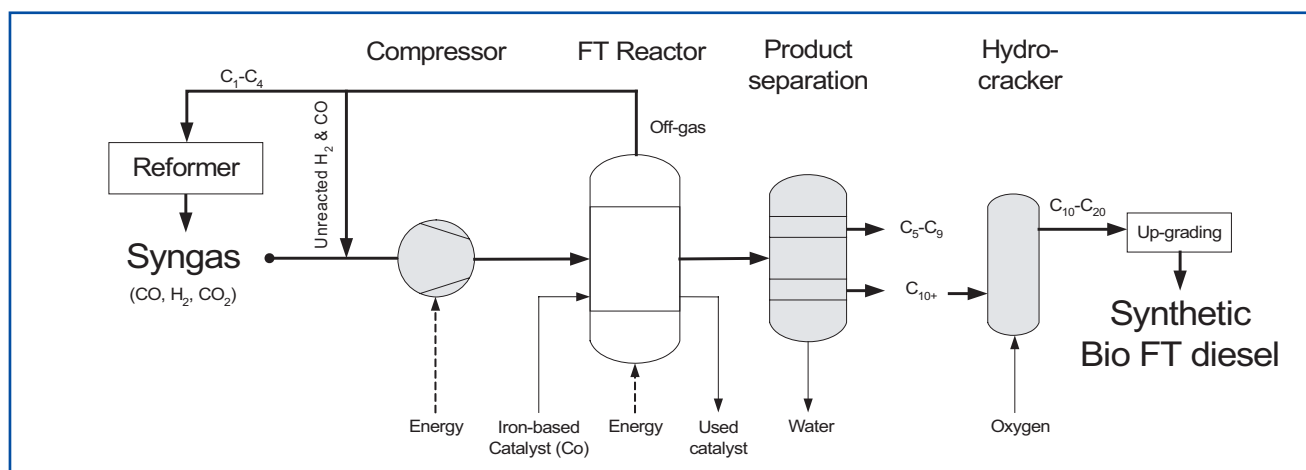

Figure 5: Process flow diagram for syngas production.

Figure 6: Process flow diagram for synthetic bio FT diesel production using syngas as a feedstock.

McKeough and Kurkela (2007) assessed the performances and costs of producing several alternative biomass-derived syngas derivatives. This comparison included FT liquids, methanol, synthetic natural gas (SNG), and hydrogen. An important characteristic of the FT conversion is the generation of high-grade by-product energy. Assuming the integration of the FT process with other energy-consuming plants, such as a paper manufacturing facility, results in the highest overall efficiency of the four alternatives.

FT fuels can be used neat without engine modifications or can be blended in any proportion with conventional diesel fuel. The properties of FT fuels can be varied depending on the FT process and the up-grading of the fuel. However, regardless of feedstock or process, FT fuels have a number of desirable properties for use in diesel engines. Some important properties for conventional diesel and FT fuels are compared in Table 4. FT fuels are liquid at ambient conditions and can be applied to the existing infrastructure (Hamelinck et al., 2004). The energy density of FT fuel is comparable to conventional diesel. Further benefits are low contents of sulphur and aromatics. Due to the typical cetane number of 50-75, FT fuels have good autoignition characteristics (Norton et al., 1999). However, lubricity of FT fuels is generally poor. A study carried out by Alleman and McCormick (2003) reveals that the cetane number influences the cold flow properties of the FT fuel. Fuels with a high cetane number, such as 75, have less desirable low temperature properties, whereas moderate cetane fuels have cold flow properties more typical of conventional diesel fuels. Yet, the lubricity of FT fuels can be improved by means of additives.

It is generally agreed that the thermal efficiency for a conventional engine fuelled with FT diesel is the same as that for the conventional engine using petroleum diesel fuel (Gaines et al., 1998; Brinkman et al., 2005). Environmental benefits of FT diesel use are emission reductions for hydrocarbons, carbon monoxide, NO_x, and particulate matters (Alleman and McCormick, 2003).

Table 4: Chemical properties of conventional diesel and FT fuels

Chemical properties	Diesel	FT-diesel
Density (kg/m³)	840 [1]	804 [2]
Lower Heating Value (MJ/L)	36.4 [1]	35.1 [2]
Cetane	49 [3]	50-75 [3]
Oxygen content (% per weight)	0 [3]	1.6 [3]

[1] ORNL, 2007; [2] Kohl 1999; [3] Norton et al., 1999.

FT technologies have been commercialised by Shell (Malaysia) and Sasol (South Africa) using natural gas and coal as a feedstock respectively (Boerrigter and Uil, 2002). However, synthetic bio FT diesel is not yet commercially installed. Current conversion technologies are not economically competitive with fossil diesel which is mainly due to the biomass gasification and gas cleaning steps (Hamelinck et al., 2004). Nevertheless, Ree et al. (2005) and Hamelinck et al. (2004) also point out that technological improvement, decreasing biomass prices and increasing oil prices may lead to feasible FT diesel production in the long-term. Increasing conversion efficiencies can also be achieved by scaling up the processes. However, it must be considered that plant scales have to be compatible with possible volumes of biomass supply for a certain region.

In a joint project, the Energy Research Centre of the Netherlands (ECN) and Shell have assessed options for an integrated biomass gasification and Fischer-Tropsch (BG-FT) system. A project is supposed to optimise the developed tar removal technology in order to create a conceptual design for a biomass gasification pilot plant (Boerrigter, 2004).

3.4. Methanol

Methanol (CH_3OH) is produced by methanol synthesis reaction from syngas feedstocks. Sources are mainly natural gas, but also coal and biomass may be considered. It is made in very large quantities for many different purposes in the chemical industry. Methanol synthesis is a combination of the Water-Gas-Shift (WGS) reaction and the hydrogenation of CO_2 using a catalyst. Both reactions are exothermic. Thus the reactors must efficiently remove the heat. Distillation is also needed to separate methanol from water, a by-product of the methanol synthesis (Huber et al., 2006). The methanol may be further converted into dimethyl ether as shown in Figure 7.

Methanol can be used directly as a transportation fuel in combustion engines or as a feed for methanol fuel cells but constitutes a very limited share in current vehicles. In Europe, the blending limit is 3% by volume in gasoline. Benefits include increased octane number, improved overall emission quality (less carbon and hydrogen, more oxygen), and a higher thermal efficiency than fossil transportation fuels (Balat, 2005). Drawbacks of methanol use are the significantly lower energy content in the fuel compared to gasoline, its high toxicity, and the increase in combustion emissions of NO_x and formaldehyde (US DOE, 2007a). According to Borgwardt (1998), methanol produced in a combined process using both biomass and natural gas as a feedstock reduces greenhouse gas emissions, is cost-competitive with petroleum fuel, and is compatible with vehicle technologies including fuel cells. Another approach to reduce production costs and to bridge the time until commercial bio-methanol plants are economically feasible is to integrate a gasification plant in a pulp and paper mill. This offers the advantage
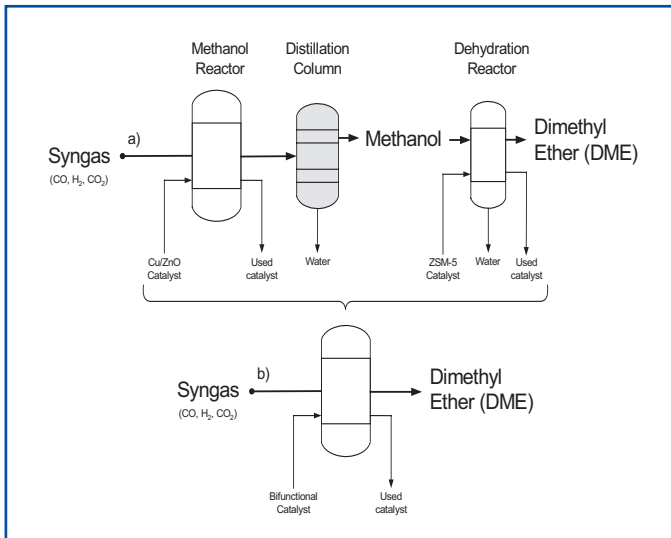
Figure 7: DME production via Methanol synthesis in a separate reactor (a), and by using a single reactor (b).

of providing a low cost black liquor as a feedstock which has been assessed in a technical and commercial feasibility study (Ekbom et al., 2003).

3.5. Dimethyl ether (DME)

DME (CH_3OCH_3) is a synthetic fuel derived from coal, natural gas, or biomass. It is a multipurpose energy carrier that can be used as a residential fuel (for heating and cooking), as a gas turbine fuel (for power generation), as a feedstock for fuel cells, and as a high quality fuel in diesel engines (Semelsberger et al., 2006).

DME has traditionally been produced in a two-step process where syngas from coal or natural gas was converted into methanol followed by its dehydration (Ge et al., 1998). Research has been carried out with the aim of simplifying these processes by applying bi-functional catalysts which can produce DME directly from the syngas. These catalysts have two active sites: one is for methanol formation and the other for methanol dehydration (Sofianos and Scurrell, 1991; Ge et al., 1998). Processes using bi-functional catalysts are currently being commercialised (Semelsberger et al., 2006). Both production pathways, with methanol as an intermediate (a) and its direct conversion into DME (b), are summarised in Figure 7.

Production of DME to substitute for diesel fuel has been promoted during the past 10 years, but plants are only economically viable where natural gas can be obtained at low price. Another challenge is the high capital cost for dedicated biomass-based DME plants. Again, integrating the gasification unit into a pulp and paper mill reduces feedstock costs. The feasibility study by Ekbom et al. (2003), which has been mentioned for methanol earlier, also addresses DME.

DME offers several advantages over conventional diesel and other transportation fuels. It can be used directly in diesel engines where it produces lower NO_x and SO_x emissions than conventional diesel and no soot. DME emits the least well-to-wheel greenhouse gases compared to synthetic bio FT diesel, biodiesel, methanol, methane, and ethanol. While DME can also be utilised as a feedstock for fuel cells, its infrastructure is less cost intensive than that for hydrogen because DME can use the existing Liquefied Petroleum Gas (LPG) and natural gas infrastructures for transport and storage. The disadvantages of DME are due to its physical properties. DME is gaseous under normal pressure and temperature which implies the need for a new distribution infrastructure. When used as a diesel fuel, the vehicle requires a fuel storage tank twice the size of a conventional diesel fuel tank because of the lower energy density. The relatively low viscosity causes leaking in pumps and fuel injectors. Ongoing research

is addressing how to increase lubricity of DME which is needed to prevent pumps and fuel injectors from failure (Semelsberger et al., 2006).

DME is not currently produced from syngas although in Sweden Chemrec and Volvo are planning to achieve this by 2008 via black liquor gasification (Ekbom et al., 2005). Trucks by Volvo will be fuelled with DME to test its properties. A pilot plant has already started to produce DME from biomass. The syngas-to-DME route faces the challenge of low H_2/CO ratio. The large excess of carbon in the form of carbon dioxide in the syngas must be supplemented with H_2. Wang (2007) investigated the technical feasibility of adding biogas which contains methane and hydrogen in order to optimise the composition in the syngas.

## 3.6. Bio synthetic natural gas (Bio-SNG)

Bio-SNG is natural gas derived from biomass via thermochemical conversion. The gas contains mainly methane, but also small amounts of hydrogen, carbon dioxide, and nitrogen. Bio-SNG production includes mainly biomass gasification with downstream methanation of the syngas. During methanation, CO and CO_2 react with H_2 to produce methane (CH_4) and water. Prior to methanation, some CH_4 can already be obtained in the gasification step, if an indirect gasifier is used (Deurwaarder et al., 2005). The two most important conversion routes for bio-SNG comprise co-production of synthetic bio FT fuels and bio-SNG, and stand-alone bio-SNG production. A third pathway for bio-SNG production is biomass gasification in supercritical water, but the composition of the syngas makes this route less favourable for bio-SNG production. Depending on the gasification temperature, gasification in supercritical water is more suitable for hydrogen production (Mozaffarian, et al., 2004).

A system for the co-generation of synthetic bio FT fuels and bio-SNG is depicted in Figure 8. The off-gas from the FT reactor is used for bio-SNG production through methanation. Bio-SNG production from off-gas alone would result in relatively small bio-SNG output. Additional bio-SNG can be generated by 'integrated co-production', in which a side-stream of the product gas of the gasifier is used for dedicated methanation. This route has been found to be the optimal system for co-production in terms of conversion efficiency and costs (Zwart and Boerrigter. 2004). A nickel-based catalyst is used for methanation. The methanation process is strongly exothermic. Therefore, heat has to be removed from the reactor, and the methane must be cooled before storage (Deurwaarder et al.. 2005). Gas cleaning is the major technical challenge for bio-SNG production, as the methanation catalysts are very sensitive to impurities (Mozaffarian et al., 2004).

Goeteborg Energi AB is currently planning to build a demonstration plant in Sweden. The facility is intended to transform forestry residues into bio-SNG while using the waste heat for district heating (Goeteburg Energi, 2007). In Europe, bio-SNG can be transported through the existing dense gas infrastructure. A future application for bio-SNG is the use as a transportation fuel, similar to compressed natural gas (CNG) and
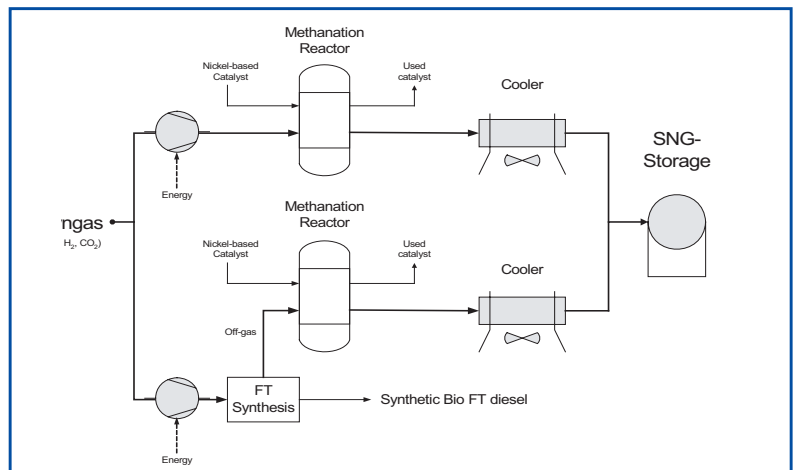
Figure 8: Process flow diagram for co-production of bio-SNG and synthetic bio FT diesel.
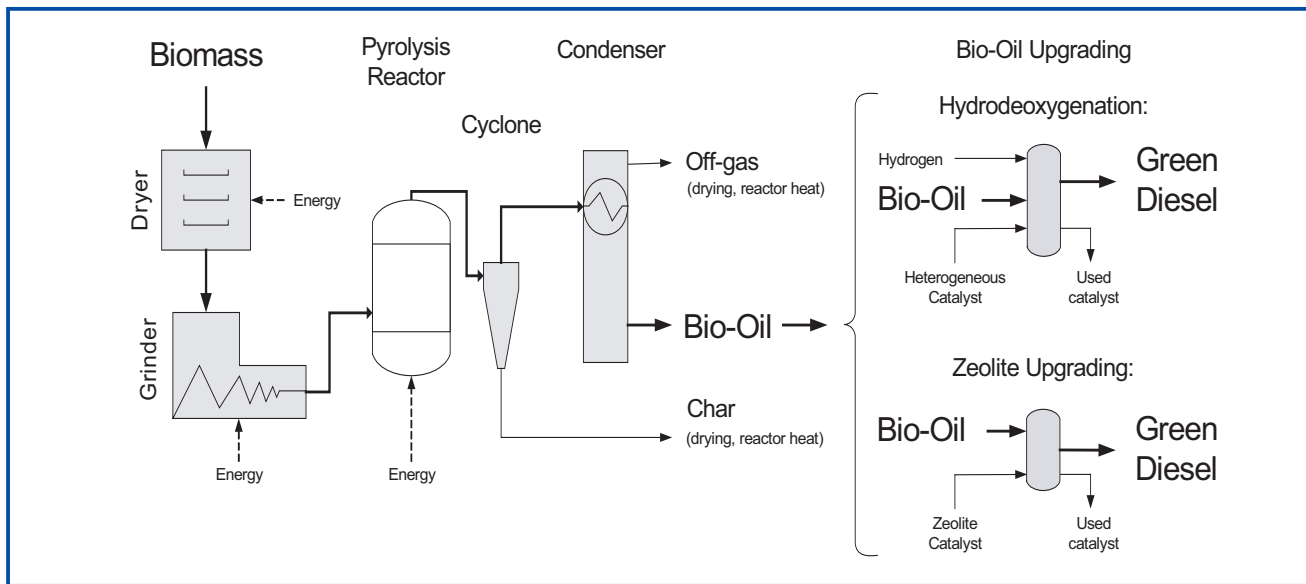
Figure 9: Process flow diagram for green diesel production from pyrolysis.

liquefied natural gas (LNG) (Mozaffarian et al. 2004). For automobile applications, bio-SNG must be compressed or liquefied to reduce its volume which requires the use of energy. However, combustion of CH_4 significantly lowers the amounts of harmful emissions such as CO, CO_2, NO_x, and particulate matter (US DOE. 2007a).

3.7. Green pyrolysis diesel

Green diesel derived from pyrolysis is made when biomass is thermally decomposed in the absence of oxygen and followed by an up-grade step. As during gasification, the thermochemical treatment of the biomass results in a wide range of products depending on the reaction parameters. Process conditions that favour liquid products are short residence time, fast heating rates, and moderate temperatures (Huber et al., 2006). Fast pyrolysis occurs in a few seconds or less with the process parameters being carefully controlled. Hence, biomass particles have to be heated quickly to the optimum temperature. The pyrolysis vapours are then rapidly cooled to give the bio-oil in order to prevent further reactions and cracking. After fast pyrolysis, char must be separated from the liquid in a cyclone since it would otherwise cause downstream processing problems.

The char can undergo steam reforming to produce syngas that is burned to run the process (Bridgwater, 2007). The off-gas, which is not converted into bio-oil, can also be burned as a fuel. Up-grading

of the product is necessary because of the heterogeneity of the bio-oil which makes it unsuitable for diesel engines. Up-grading encompasses a variety of pathways including hydrodeoxygenation and Zeolite up-grading, both converting the bio-oil into a fuel which can be used directly in diesel engines. High pressure hydrogen is needed during hydrodeoxygenation and the added cost represents an economic disadvantage over Zeolite up-grading. However, bio-oil that is processed using a Zeolite catalyst results in poor hydrocarbon yields. An overview for this process is given in Figure 9.

Bio-oils can also be blended into diesel fuels using expensive surfactants, thus reducing undesirable viscosity characteristics. Another pathway is steam-reforming which breaks the chemical structure of the bio-oils into a different source of energy. Steam reforming of bio-oils produces syngas which can then be converted into a range of fuels. This is associated with the opportunity for the bio-oils to be produced in smaller plants while the bio-oils are transported to a large central biorefinery where they are converted into syngas-derived fuels. The concept is based on cost savings by transporting energy-dense bio-oil rather than transporting the less dense biomass (Huber et al., 2006).

As mentioned earlier, bio-oils are not directly suitable as a transportation fuel. The performance of bio-oil as a fuel in a direct injection diesel engine was tested in a study by Shihadeh (2000).

Table 5: Biomass-to-biofuel conversion technologies: current development stages[#].

Technologies	Laboratory	Pilot Plant	Demonstration Plant	Market
Sugar/Starch ethanol				
Lignocellulosic ethanol				
P-Series				
Biodiesel & HDRD				
Syn. bio FT diesel				
Methanol				
DME				
Biomethane				
Bio-SNG				
Green pyrolysis diesel				

[#]**HDRD:** Hydrogenation derived renewable diesel (i.e., NExBTL)   **DME:** Dimethyl ether   **Bio-SNG:** Bio-Synthetic natural gas

On the one hand, it was found that the thermal efficiency of the two tested bio-oils equalled that of the diesel fuel. On the other hand, both bio-oils exhibited excessive ignition delays and autoignition must be supported by combustion air preheating which required modifications on the test engine. Up-grading, either via the syngas conversion route or by hydroprocessing, is therefore necessary.

Green diesel from pyrolysis oil is not a commercial product at the moment, but there is a growing interest in producing liquid transportation fuels using fast pyrolysis which is a relatively new technology for converting biomass (Bridgwater, 2007). Several pilot plants for the development of fast pyrolysis have been build in the past years in Germany, Brazil, and the USA (Bridgwater, 2004). Pyrolysis oil, or bio-oil, is commercially used as a boiler fuel for stationary power and heat production, and for chemical production (Huber et al., 2006). An important economical challenge for producing green diesel is reducing the capital cost of up-scaling the facilities (Bridgwater, 2007). However, there is a potential that pyrolysis oil could be processed with some modifications by existing oil refineries which is currently being investigated in joint programmes between industry and government (US DOE, 2006; Biocoup, 2007).

4. IMPACT OF R&D ON ACCELERATING THE USE OF SECOND-GENERATION BIOFUELS

The biomass-to-biofuel conversion technologies described in Sections 2 and 3 are currently at different stages of development. The conversion of oil seeds into renewable diesel has been commercialised in many countries, whereas hydrolysis and fermentation of cellulose into ethanol has not yet been demonstrated to be economically viable in a large-scale facility. The development stages of current conversion technologies are summarised in Table 5. The high efficiencies of commercialised technologies are due partly to improvements that result from a learning curve in large-scale plants. Therefore, the production efficiencies of cane/corn-ethanol, biodiesel, and biomethane are more exploited than the non-commercialised technologies. The efficiency improvement potential is therefore higher for second-generation biofuel technologies such as cellulose ethanol, P-Series fuels, synthetic bio FT diesel, and DME. Further attention in research should be drawn to these technologies.

Second-generation biomass-to-biofuel technologies are characterised by a complex set of energy transformation steps as described in Section 3. It is typical for all transformation processes that they face technical problems at the interfaces between the consequent process steps – that is, from biomass pre-treatment to obtain a feedstock with well-defined physiochemical properties that can be fed into the conversion reactor, the purification, and subsequent upgrading of the reaction products to a quality that can be treated by catalytic or enzymatic reactors without detrimental effects on the catalyst and enzymes. Furthermore, it includes the final purification process for the biofuels to be marketed under well-defined fuel quality specifications and standards developed by the standardisation bodies.

The complexity of energy transformation along with the risk involved in the investment in new technologies are two of the major reasons why second-generation biofuels are not yet commercialised. The purpose of research and development in this field is to mature the technologies in order to facilitate the implementation of second-generation biofuels on the transportation fuel markets worldwide. However, the efforts made for research and development should be focused on areas which promise to have the greatest impact on a set of important criteria. The aim of this section is to introduce these criteria and to highlight their relevance for the future biofuel economy. A systematic approach is used to track the possible impacts of research and development.

The key to identifying research gaps is understanding the science and technology of transformation and then applying systematic analysis to determine the impact on important technical, economical, and ecological barriers. Criteria that indicate benefits and costs have to be found. For example, each transformation step has a specific impact on the overall production cost of a certain biofuel. In order to reduce costs, it is essential to identify the critical technological steps (e.g., the cost-effective use of
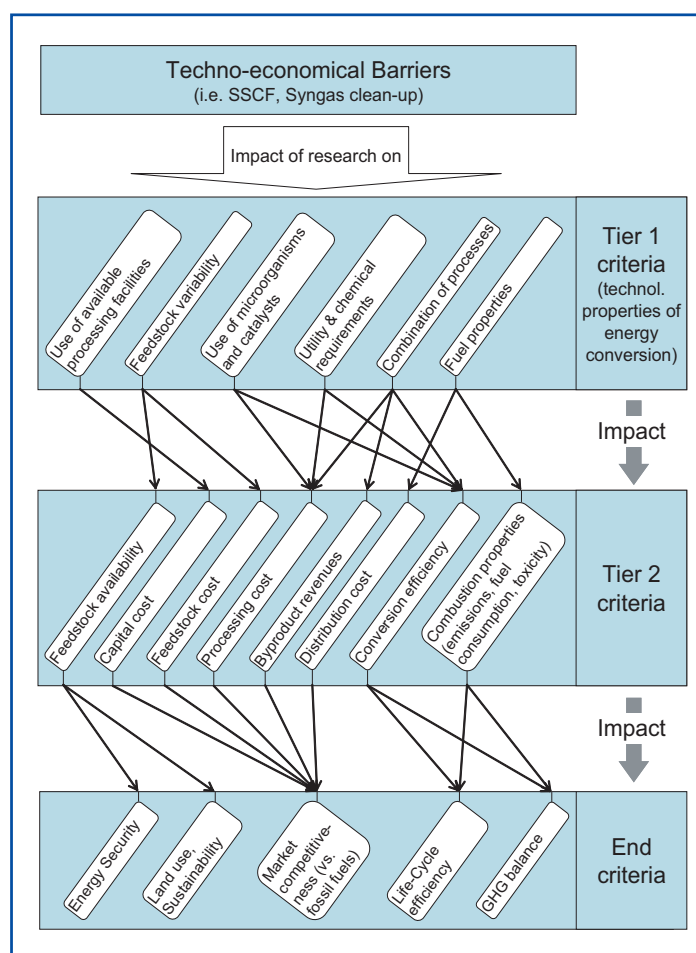
Figure 10: Relationship between different criteria for the evaluation of R&D topics

enzymes) which have the greatest effect on the overall economics. Once these criteria are identified, they will serve as a basis to evaluate the priorities of topics in research and development.

Figure 10 represents the most important criteria that must be taken into account in order to evaluate key topics in research and development. It also displays the relationship between the different criteria which are not independent. The criteria are divided into three levels. The first set of criteria (Tier 1) form the technological characteristics of the conversion of biomass into biofuels, no matter which technologies are applied. For example, all technologies require utilities. However, the parameters and values for these characteristics are different for each conversion technology. For example, feedstock preparation may involve hot water pre-treatment for the cellulose-to-ethanol process where heat is used mainly as a utility. For gasification technologies, the main utility for feedstock preparation required is electricity for size reduction. These differences among second-generation biofuel technologies have to be assessed according to their significance in the overall scheme (Figure 10). The Tier 1 criteria have a direct impact on the Tier 2 criteria which then bear upon the End criteria. The End criteria represent the main drivers for the commercialisation of second-generation biofuels.

The Tier 1 criteria are:
• the possibility of using already available processing facilities (with minor or no modifications),
• feedstock variability,
• the necessity of using either enzymes, bacteria, or catalysts to run the processes,
• stability of the processes,
• utility requirements,
• the technological feasibility of combining different biofuel conversion processes, and
• the chemical and physical properties of the produced biofuel.

4.1. Use of available processing facilities

This criterion draws upon the fact that building new processing facilities involves high capital cost. These costs can be reduced, if already available processing facilities are adapted to new technologies. Fewer capital costs results in lower overall production cost which increases market competitiveness with fossil fuels. In turn, this will help accelerate the commercialisation of the respective technologies. Applications include the biochemical and thermochemical conversion route. There are plans to convert corn-to-ethanol plants into cellulose-to-ethanol plants. A first such facility in the USA is planned to start production in 2009 (US DOE, 2007b). With regard to fast pyrolysis, efforts are made to convert bio-oils into diesel fuel using existing oil refineries as described in Section 3.7. These efforts should be supported in the future.

4.2. Feedstock variability

It is desirable that processing technologies can convert a variety of different biomass feedstocks into biofuels. The more feedstocks are applicable for biofuel production, the more feedstock will be available in a certain region or country. A larger amount of available feedstock will increase the potential output in biofuel production which results in greater energy security. In addition, fewer areas of land will be needed to grow energy crops which makes biofuel production more sustainable. The performances of pre-treatment and feedstock preparation are very critical for using different kinds of feedstocks. Research is therefore necessary to improve these conversion steps.

4.3. Use of enzymes, bacteria, or catalysts

Biomass-to-biofuel conversion involves the application of micro-organisms, such as yeast and bacteria (biochemical route), and/or catalysts, such as enzymes (biochemical route) or metallic catalysts (thermochemical route). For both routes, a choice of micro-organisms and/or catalysts has to be made in terms of type and quantity as this has an impact on conversion rates and process stability. Due to their currently high production cost, the use of enzymes (for pre-treatment and hydrolysis) and micro-organisms (i.e., bacteria suitable for SSCF) drives the processing cost for cellulose ethanol production. During gasification of biomass, the optimal use of catalysts has an influence on the quality of the produced syngas. If impurities (i.e., tars) in the syngas can be reduced, downstream problems diminish and fuel quality increases. Therefore, research for the development and improvement of micro-organisms and catalysts is needed to reduce processing costs. Furthermore, improvement in this field may lead to an increase in conversion efficiencies.

4.4. Utility and chemical requirements

All described technologies require utilities and chemicals such as electrical power, heat, and/or oxygen and hydrogen to process the biomass into the desired form of energy. These inputs have a direct impact on both processing costs and conversion efficiencies. Therefore, efforts are made to reduce utilities and the use of chemicals to a minimum. Current challenges in this area for cellulosic ethanol production are particle size reduction and pre-treatment where large amounts of electricity and heat are necessary. For gasification technologies, the use of oxygen drives the processing costs as well the required energy for feedstock drying and particle size reduction. Furthermore, an unsolved issue is how to use the low temperature heat during the FT process. It is worth noticing that the optimal application of utilities and chemicals is also an engineering issue which can be optimised efficiently in (pre-)commercial-scale facilities. A further shift in efficiencies can therefore be expected once the first commercial-scale plants have started production. A decrease in required utilities and chemicals will not only improve market competitiveness of the produced fuel. The greater conversion efficiency will also improve the fuel's life-cycle efficiency and greenhouse gas balance.

4.5. Combination of processes

A number of examples throughout Section 3 have shown the efforts that are made to combine different processing technologies in a single facility. For instance, the conversion of lignocellulosic biomass into ethanol can be combined with animal feed production in a dry mill plant which improves market competitiveness through by-product revenues. Another example is the integration of biomass gasification and FT synthesis into a large paper manufacturing plant which can consume parts of the energy released during the FT process. This will reduce processing costs and improve conversion efficiency, if progress in research can make the combination of processes technologically feasible.

4.6. Fuel properties

It has been outlined that the chemical and physical properties of biofuels vary according to the different processing technologies. All biofuels are generally less hazardous than conventional fuels when exposed to the environment. However, the chemical composition is directly related to pollutant emissions and fuel consumption in the 'tank-to-wheel' stage of the fuel's life-cycle which influences the overall efficiency and the greenhouse gas balance. Most of the second-generation biofuels discussed throughout this paper can be used in current vehicle technologies without or with only minor modifications.

Today's engines are not optimised to these new fuels to improve the thermal efficiencies during combustion. Research in this field is likely to improve the biofuel's life-cycle efficiency and greenhouse gas balance. The physical properties, such as density and condition at atmospheric pressure, indicate how suitable a biofuel is for use in the current infrastructure. This encompasses the distribution of the fuel from the plant to the end customer, including fuel storage along the distribution chain and inside the vehicle tank. While distribution systems are available for both gaseous and liquid fuels, gasoline and diesel-like fuels benefit from the fact that they can be stored more easily and at lower costs than gaseous fuels. Furthermore, the quality of the biofuel is also a regulatory issue. In order to commercialise a new type of fuel, it has to pass an authorisation process and meet certain standards. This also has an impact on the maximum amounts which can officially be blended into conventional fuels.

5. RESEARCH GAPS: PRIORITY EVALUATION OF EXISTING AND PROSPECTIVE R&D EFFORTS

The production processes of the second-generation biofuels and the associated techno-economical barriers have been outlined. Furthermore, the criteria with the greatest impact on the acceleration of using second-generation biofuels are indicated to give a basis upon which research priorities and gaps may be identified. This section presents the R&D gaps and priorities that have been identified by the project participants and for which background information is given throughout this publication. More research topics have been identified for biofuel technologies in the respective sections.

5.1. Lignocellulosic ethanol

The effective combination of pre-treatment, hydrolysis, and fermentation of lignocellulosic material is a key to economic cellulosic ethanol production. Pre-treatment currently determines the efficiency with which processing steps, downstream of pre-treatment, are able to convert cellulose and hemicellulose to hexoses and pentoses. Pre-treatment overcomes the recalcitrant nature of lignocellulose by opening its structure and enabling enzymes to access the cellulosic fraction. Further research in this field is needed to improve the efficiency of pre-treatment, reduce the cost of enzymes used for hydrolysis by modifying the enzymes and combining hydrolysis with fermentation, and developing micro-organisms that are able to effectively utilise both hexoses and pentoses to produce ethanol. This research is receiving significant governmental support. Nonetheless, studies of the individual biocatalytic steps as well as the systems

integration of the biology and engineering into effective processes represent a gap that must continue to be addressed if the economical production of ethanol from cellulosic feedstocks is to be achieved.

5.2. Green diesel derived from Fischer-Tropsch synthesis

In thermochemical conversion, Fischer-Tropsch (FT) synthesis promises high potential because it gives a liquid with superior fuel properties for use in diesel engines. Research is needed to improve the economics of the process. A major research gap exists in studies that address longevity and robustness of the catalysts, as well as more cost-effectively achieving clean-up of the syngas. Research to fill this gap is needed to improve the quality of the feedstock for FT synthesis and to reduce the down-stream costs for equipment and processing both due to clean-up of the product and systems that guard the catalysts from potential poisons that reduce their life. For the development of FT synthesis, knowledge about kinetic principles of catalytic conversion is necessary. Catalysts specifically designed for FT synthesis of feedstocks derived from renewable resources are needed to increase the desired liquid fuel yields.

5.3. Green pyrolysis diesel

Pyrolysis of biomass provides the opportunity to convert plant matter into a dense bio-oil which can be transported over long distances. Further processing of the bio-oil in modified but existing oil refineries could reduce capital cost and the cost for additional infrastructure. However, research gaps exist in the development of stabilisers for the oils so they are not too viscous during transport, and improvements in catalysts so that oils are formed that are more stable in the first place. Research is needed to target the improvement of the catalytic conversion so that the bio-oil exhibits stability over time, which is a requirement for long-distance transport.

5.4. Dimethyl ether (DME)

The production of dimethyl ether has potential research gaps in addressing developing robust catalysts that are able to handle the type of syngas that might result from biomass. Gas clean-up so that the catalyst is not deactivated by inhibitors and catalyst poisons is important. DME production from renewable resources would depend on the gas that is derived from biomass having a similar composition to natural gas, and a price that is less than that of natural gas. The capital costs of building a biomass to DME facility are high. This is a common denominator with the

other types of second-generation fuels as well. However, perhaps the largest gap relates to the infrastructure that would be needed to deliver DME as a transportation fuel. DME is gaseous under atmospheric pressure and temperature ranges. An additional distribution infrastructure will therefore be needed to deliver DME to the diesel transportation system. Vehicle modifications would also be required since this fuel's lower energy density would require a fuel storage tank twice the size of a conventional diesel fuel tank for the same driving distance.

5.5. P-Series fuels

The research gap for P-Series fuels relates to development of the catalyst and control of the reactions to obtain high yields. The catalysts that are likely to be used to generate furfural or other aldehydes, and levulinic acid (from glucose) will need to be developed further. Catalyst stability and resistance to poisons that would decrease catalyst activity are needed to enable development of industrially robust catalysts. The research gaps are similar to cellulose ethanol in that a cost-effective source of relatively pure sugars will be needed for the production of MTHF.

There are two other categories of research gaps which were not addressed in great detail by this publication but are important, nonetheless. These are given in Sections 5.6 and 5.7.

5.6. Engines

Life-cycle efficiencies of all second-generation biofuels depend on the performance of the fuels in the engine. However, the majority of the current vehicle engines are not optimised for the efficient utilisation of biofuels. Engine modifications are needed to enable the second-generation biofuels to be suitable in terms of combustion characteristics and mileage. In order to enhance competitiveness of biofuels, it is necessary to accelerate the development of appropriate engine technology.

5.7. Hybrid fuels

The composition of hybrid fuels can be varied, which makes them more flexible for use than a single type of biofuel. Mixtures can be adjusted to climatic conditions and a greater variety of feedstocks in a certain region can be utilised. However, these fuels and the amounts that are blended must be specifically characterised to give optimal fuel properties and to meet national regulations. Furthermore, policies should give a framework so that the development of hybrid fuels can be targeted precisely.

The Abengoa Bioenergy's straw to ethanol demonstration facility in Salamanca, Spain. Courtesy R. Wooley, Abengoa, USA.

6. RECOMMENDATIONS: FUTURE STEPS NEEDED TO CLOSE THE KNOWLEDGE GAP

There has been a re-invigoration of research efforts that address biofuels, with respect to both bio-processing and thermal processing. These efforts are supported through federal funding in the USA and Europe, as well as significant extramural and intramural research funding through various oil companies including Exxon Mobil (at the California Institute of Technology), BP-Amoco (University of California, Berkeley and University of Illinois, Urbana-Champaign), Shell (Iogen Corporation), Chevron (University of California, Davis), and others. In the USA, the Department of Energy is making a billion dollar investment in fundamental research that addresses topics ranging from genomics applied to development of energy crops with enhanced post-harvesting processing properties, development of yeast and bacterial systems that are genetically modified for enhanced production of enzymes, more efficient processing of glucose, xylose, and other sugars, to ethanol, and multifunctional microbial systems that consolidate saccharification capability with multi-substrate fermentative micro-organisms (referred to consolidated bio-processing).

In addition, previous and planned research initiatives in reducing enzyme costs and enhancing hydrolytic and transformative capabilities of enzymes is being pursued both in the USA and in Europe, also under government funding. In the thermal and bioprocessing of oils to diesel, generation of synthesis gas from biomass sources, FT synthesis of diesel substitutes from feedstocks derived by thermal processing of biomass, VTT Finland, the United Kingdom, and the European Union are making major investments. In Germany, Choren Industries is making joint efforts with Shell, Volkswagen, and Daimler to commercialise FT technologies (NNFCC, 2007a). The Netherlands and Greece are providing industrial and research incentives for thermal processing research to form green diesel and the development of enhanced microbial biocatalysts for hexose/pentose fermentation. A recently announced set of centres under the Genomes to Life (GTL) initiative of the Office of Science of the US Department of Energy is addressing key challenges in the plant biosciences, microbial development, and consolidated bio-processing approaches. These centres are being started up at the University of California, Berkeley/Lawrence Berkeley National Laboratory, the University of Wisconsin, Madison & Michigan State University, East Lansing, and the University of Tennessee/Oak Ridge National Laboratory. These centres provide a location, infrastructure, and critical mass for biological research related to biomass conversion by combining the important competencies of DOE National Laboratories, and co-located universities or industry.

Given this wide range of efforts that will hopefully continue to expand, it might appear that research gaps would be difficult to identify. However, on the contrary, this project team found a number of very important gaps. Some are related to government policy and incentives which are outside the scope of the study. Other gaps are analysed and covered by reports from Task 39 of IEA Bioenergy. Comprehensive views on biofuels are given by the European Commission (VIEWLS, 2005), and the US Department of Energy (Houghton et al., 2006). The current Task 41, Project 2 did, however, identify some important research gaps. These are in bio-processing and thermochemical conversion, and coincide with recommendations of other reports, mentioned earlier in this section. These gaps are divided into bio-processing and thermal processing.

The bio-processing of cellulosic materials has significant potential, but key impediments exist for the economically attractive implementation of processing technology that would convert a solid cellulosic feedstock into a liquid fuel. These include pre-treatment, the cost of enzymes, fermentation of a range of substrates to ethanol, and reduction of capital as well as operating extents. This project identified cellulose pre-treatment as a research gap. While a number of research initiatives are examining the effect of hydrolysis on cell wall structure, research on pre-treatment that economically modifies this structure to improve downstream processing is needed. Significant research that is addressing modification and imaging of cell walls is under way. However, the proactive study of how mechanical, thermal, and/or

The system for thermal processing of biomass being explained to IEA Bioenergy ExCo visitors by Calvin Feik of NREL. Courtesy L. Russo, USDOE.

aqueous media can be directed to modify cell wall structure is now needed. This includes fundamental research on physical parameters that change upon pre-treatment, and the mapping of these conditions on to optimal conversion strategies in a systematic manner. Furthermore, development of existing equipment or new processing units is needed so that laboratory discoveries may be developed, tested, and translated into large-scale unit operations upon which a cellulosic ethanol industry will be built.

Research gaps in thermal processing exist in the post-reaction processing of gases or oil from gasification and pyrolysis systems, respectively. The formation of these products is a first step, in that it will provide feedstocks for catalytic conversion processes that generate liquid transportation fuels. A recent paper (McKeough and Kurkela, 2007) identifies some of these issues and also reports industrial scale experience that leads to the conclusion that this type of liquid fuel may be produced at 0.50 Euro/litre (or approximately US$2.65/gallon[1]). Some of the key steps that require research are gas clean-up to remove colloidal dust and volatile organics that quickly foul, and limit the lifetime of FT or synthesis gas catalysts. In this case, the exact nature of the inhibitors, relative to their separation characteristics must be determined, and robust methods of gas clean-up determined. This has also been noted by SenterNovem in the Netherlands. Furthermore, the research and development of catalysts that are designed specifically to be used with synthesis gas for FT synthesis is needed, and in some respects reflects a corollary approach for research for developing enhanced enzymatic and microbial biocatalysts for cellulose ethanol production. From a fundamental research perspective, the production of biodiesel was considered to be based on established technologies and did not have identifiable research gaps. Although an improvement in this technology is a subject of continuing activity, biodiesel itself is already a commercially available product, much like ethanol from sugarcane or corn. In comparison, FT liquids, green diesel, and cellulose ethanol have tremendous potential and also major technical challenges to be addressed.

Co-processing of fuels (i.e., first-generation biofuels and fossil fuels) or integrating second-generation biofuel technologies in suitable industrial applications (e.g., to reduce capital cost) can be considered as a short-term solution to accelerate biofuel production. Co-processing and integration will push efforts to develop commercial scale biorefineries capable of using a variety of feedstocks while offering product flexibility (NNFCC, 2007a). In the long-term, it is essential to promote the fundamental research in order to continuously improve the technical and economical feasibility of second-generation biofuels. Current research investments are targeting all these challenges. This publication has identified gaps within these areas which must be addressed to more quickly move the product from the laboratory to the billion gallon scale that represents the daily international consumption of liquid transportation fuels currently derived from petroleum.

[1] one gallon = 3.785 litres

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8. GLOSSARY

BG-FT	Biomass Gasification and Fischer Tropsch
Bio-SNG	Bio Synthetic Natural Gas
BTL	Biomass to liquid
CH_3OCH_3	Dimethyl ether (DME)
CH_3OH	Methanol
CH_4	Methane
CNG	Compressed Natural Gas
CO_2	Carbon dioxide
Co	Cobalt
DME	Dimethyl ether
ETBE	Ethyl-tertio-butyl-ether
Fe	Iron
FFV	Flexible Fuel Vehicle
FT	Fischer Tropsch
H_2	Hydrogen
HDRD	Hydrogenation-derived renewable diesel
LNG	Liquefied natural gas
LPG	Liquefied Petroleum Gas
MPa	Megapascal
MTBE	Methyl tert-butyl ether
MTHF	Methyltetrahydrofuran
MW_{th}	Megawatt thermal
N_2	Nitrogen
OLGA	Oil-based gas washer
SHF	Separate hydrolysis and fermentation
SNG	Synthetic natural gas
SSCF	Simultaneous saccharification and co-fermentation
SSF	Simultaneous saccharification and fermentation
WGS	Water-Gas-Shift

Construction of a gasifier at Chippewa Valley Ethanol, a corn to ethanol facility. When this project is completed, CVEC will have replaced over 90% of its natural gas energy inputs with biomass power from corn cobs and other agriculture residues, grasses and wood. Courtesy B. Lee, Chippewa, USA.

IEA Bioenergy

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