Ethanol from Lignocellulosics:
Comparing biofuel technology options
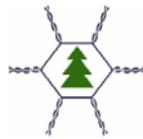A REPORT TO IEA BIOENERGY TASK 39

AUTHORS:
Mabee, Warren E.
Saddler, Jack N.

Forest Products Biotechnology

University of British Columbia

Report T39-P4   30 April 2006

Executive Summary

The global energy sector will likely change in significant ways over the course of the 21st century. Increasing volatility in the market for refined petroleum products, including transportation fuels, has spurred tremendous interest in creating a renewable and sustainable alternative that can fuel our cars and our economy. A new generation of transportation fuels based on lignocellulosic biomass are one viable option.

Previous disruptions to petrochemical supplies, such as the oil crisis of 1973, had led to the development of a first generation of biofuels, particularly sugar- and starch-based ethanol and vegetable oil-based biodiesel. These renewable transportation fuels were favoured because of their ease of use. These fuels may be distributed and sold from existing infrastructure, and when blended with conventional fuels, can be utilized within modern engines without modification. These 1st-generation biofuels have become commonplace in Brazil, parts of Europe, and in North America.

One drawback with 1st-generation biofuels is that they are they are limited by feedstock availability, and compete with food applications. Thus their overall contribution to our demand for liquid transportation fuels is reduced.

Since 1998, oil prices have again been on the rise, due to a combination of growing demand for petroleum products, increasing instability in the Middle East, and natural disasters that have adversely affected productivity. One response has been a quick expansion of 1st-generation biofuel production in some European countries, such as Sweden, Germany, and France, as well as in Canada and the United States. At the same time, other bio-based options for transportation fuels have been resurrected and re-examined. Technological advancements and innovations have provided us with pathways towards a second generation of biofuels that have the potential to replace significant portions of the world's transportation fuel demand.

This report presents two transformative technologies that could be used to expand the production of 2nd-generation biofuels, and deliver additional energy products that can maximize economic and environmental benefits to the industry. These technologies include advanced thermochemical systems that reduce wood to its most basic gaseous components through pyrolysis or gasification, and bioconversion systems that can isolate the building-block chemicals of wood.

The thermochemical platform typically uses a combination of pyrolysis, gasification, and catalysis to transform wood into syngas - the gaseous constituents of wood - and then into fuels or chemicals. Syngas production through pyrolysis is accompanied by the generation of char, which can then be gasified to provide process heat and energy for the thermochemical platform. A variety of commercial-scale processes exist to transform fossil fuels such as coal or natural gas into liquid fuels, including Fischer-Tropsch fuels. However, the use of biomass instead of fossil fuels changes the composition of syngas, creating a more heterogeneous intermediate product and increasing the difficulty in downstream catalysis. A range of technical problems must be overcome before biomass becomes a commercially-viable substitute for fossil feedstocks in 2nd-generation biofuel production. However, elements of the thermochemical platform are highly suitable for bioenergy production.

The bioconversion platform typically uses a combination of physical or chemical pretreatment and enzymatic hydrolysis to convert lignocellulose into its component monomers. Once liberated, the carbohydrate components of wood may be processed into a number of chemical and fuel products. A number of US-led projects are paving the way for new chemical products from the lignocellulose-based biorefinery, including bioethanol, lactic acid and polylactide, propanediol, and succinic acid. Cellulosic-based bioethanol from a demonstration-scale plant in Ottawa is already being produced and blended as an oxygenate in fuels. Other chemical products can be

used to create consumer products such as bioplastics, or as platform chemicals in a number of industrial applications. The development of better ways to separate lignin from the lignocellulose matrix during bioconversion has created the possibility of developing value-added lignin-based products as well. The bioconversion platform therefore has the ability to serve as the basis for full-fledged wood-based biorefining operations, generating value-added bioproducts as well as fuel and energy for the forest sector.

Using components of these platforms, forest biomass can provide a sustainable, renewable source of bioenergy. This report illustrates how evolutions in technology may be combined to create truly revolutionary processes that can transform the energy sector.   It is also shown how each technological platform might be used to generate other, valuable chemical products or energy, thus creating a biorefinery. An important conclusion is that the development of the biorefinery should take precedence over specific biofuel and bioenergy projects.

This report makes a number of key recommendations, summarized in the last section. In brief, they are as follows:

- Develop a comprehensive strategy for 2nd-generation biofuel development that includes minimizing risk for infrastructure development, as well as economic incentives for bioenergy production and consumption
- Funding for RD&D should be linked to development of biorefinery facilities;
- 2nd-generation biofuel funding should be harmonized with renewable energy programs and other synergistic programs, such as rural employment and agricultural assistance programs;
- Continue funding to address technical challenges and hurdles in the development of transformative technologies at all levels of research, development and deployment; and
- Create specialized programs to support specific 2nd-generation biofuels.

Table of Contents

List of Figures

1.　　Introduction

1.1.　　Report Overview

In this report, we examine 2nd-generation biofuels, considering both the current state of the technology and near-future technology developments.　The report focuses on lignocellulosic-based ethanol, derived through biological pathways, and 'biosyn' diesel, derived through thermochemical pathways.　We assess the ability of these technologies to provide fuels under a variety of climate-change scenarios, theoretically reducing volatility in the energy sector.　We use these scenarios to measure the ability of 2nd-generation fuels to reduce greenhouse gas emissions and improve environmental performance, increase resource sector employment, and encourage regional development.　A number of recommendations are provided to policymakers.

The report is to be submitted to the Task 39 of IEA Bioenergy.　Initial findings were presented at the Task 39 workshop in Ystad, Sweden in October 2005.　It will be reviewed by policymakers in Europe, Canada and the United States, and will hopefully provide valuable information to the industry at a crucial time in its development.　Parts of this report are being prepared for peer-reviewed publication.　This report was funded in part by the BIOCAP Canada Foundation and by Natural Resources Canada, and their contributions are greatly appreciated.

1.2.　　Task 39 Liquid Biofuels

The International Energy Agency was founded in 1974 as an autonomous body within the OECD to implement an international energy programme in response to the oil shocks. Membership consists of 25 of the 29 OECD member countries. Activities are directed towards the IEA member countries' collective energy policy objectives of energy security, economic and social development, and environmental protection. One important activity undertaken in pursuit of these goals is a programme to facilitate co-operation to develop new and improved energy technologies.　A key commitment is to affordable, renewable energy (IEA 2002).

IEA Bioenergy was created in 1978 by the parent organization with the aim of improving cooperation and information exchange between countries that have national programmes in bioenergy research, development and deployment.　Activities operating under IEA Bioenergy are set up under Implementing Agreements. These are independent bodies operating in a framework provided by the IEA. There are 40 currently active Implementing Agreements, one of which is IEA Bioenergy.

IEA Bioenergy Task 39, "Liquid Biofuels," is currently composed of 9 countries/regional associations (Austria, Canada, Denmark, European Union, Finland, The Netherlands, Sweden, USA and UK) interested in working together to successfully introduce biofuels for transportation into the marketplace. This Task reviews technical and policy/regulatory issues and provides participants with comprehensive information that will assist them with the development and deployment of biofuels for motor fuel use.

Biofuels are presently the only renewable source of liquid transportation fuels and offer many potential environmental and economic benefits. The production of the raw biomass material and its subsequent conversion to fuels creates local jobs, provides regional economic development, and can increase farm and forestry incomes. Biofuels also offer many environmental benefits including reduction of carbon dioxide emissions associated with global climate change and improved waste utilization. The chemical composition of many biofuels also leads to improved engine performance and reduces unwanted pollutants such as carbon monoxide and unburned hydrocarbons.　Billions of litres of ethanol are used annually for transportation fuels, and biodiesel is gaining in popularity in some regions.

Because the costs of biofuels are relatively high, these fuels presently have significant impact only in those locations where biomass is abundant, and where governments provide policies and

incentives that encourage their use. Ethanol from starch and grain crops is used extensively in Brazil, Canada, United States, and to a lesser extent in Sweden. Biodiesel has attracted increasing interest throughout Europe, and to a limited extent in North America. In the short term, governmental policies and incentives allow the infrastructure for biofuels to be established, and they start the transition from a petroleum-only economy. At the same time, governments are also sponsoring research and development efforts to reduce the cost of biofuels so they can compete more effectively in the marketplace. The long-term viability of biofuels will require both that the infrastructure for biofuels exists and that economically competitive processes are available. To achieve this goal, it will be necessary to deal with both the technical and the non-technical issues (i.e., policy, regulatory, legislative) relating to biofuels in a comprehensive manner.

2.   Literature Review

2.1.   Biofuel platforms

The technical platform chosen for 2nd-generation biofuel production will be determined in part by the characteristics of the biomass available for processing. The majority of terrestrial biomass available is typically derived from agricultural plants and from wood grown in forests, as well as from waste residues generated in the processing or use of these resources. Today, the primary barrier to utilizing this biomass is generally recognized to be the lack of low-cost processing options capable of converting these polymers into recoverable base chemical components (Lynd et al. 1999).

In the United States, much of the biomass being used for 1st-generation biofuel production includes agricultural crops that are rich in sugars and starch. Because of the prevalence of these feedstocks, the majority of US activity towards developing new products has focused on the bioconversion platform (BRDTAC 2002a). Bioconversion isolates sugars from biomass, which can then be processed into value-added products. Native sugars found in sugarcane and sugar beet can be easily derived from these plants, and refined in facilities that require the lowest level of capital input. Starch, a storage molecule which is a dominant component of cereal crops such as corn and wheat, is comprised wholly of glucose. Starch may be subjected to an additional processing in the form of an acid- or enzyme-catalyzed hydrolysis step to liberate glucose using a single family of enzymes, the amylases, which makes bioconversion relatively simple. Downstream processing of sugars includes traditional fermentation, which uses yeast to produce ethanol; other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream.

Forest biomass or agricultural residues are almost completely comprised of lignocellulosic molecules (wood), a structural matrix that gives the tree or plant strength and form. This type of biomass is a prime feedstock for combustion, and indeed remains a major source of energy for the world today (FAO 2005). The thermochemical platform utilizes pyrolysis and gasification processes to recover heat energy as well as the gaseous components of wood, known as synthesis gas or 'syngas'. Syngas can then be refined into synthetic fuels, including Fischer-Tropschs, methanol, and ethanol, through the process of catalytic conversion.

Lignocellulose is a complex matrix combining cellulose, hemicellulose, and lignin, along with a variable level of extractives. Cellulose is comprised of glucose, a six-carbon sugar, while hemicellulose contains both five- and six-carbon sugars, including glucose, galactose, mannose, arabinose, and xylose. The presence of cellulose and hemicellulose therefore makes lignocellulose a potential candidate for bioconversion. The ability of the bioconversion platform to isolate these components was initially limited, as the wood matrix is naturally resistant to decomposition. Recent advances, however, have made this process more commercially viable. Costs remain higher than for starch-based bioconversion, but there is added potential for value-added products that can utilize the lignin component of the wood.

In order to incorporate all aspects of biofuel production, including the value of coproducts and the potential of the industry to diversify their product offering, we employ the biorefinery concept. The biorefinery concept is important because it offers many potential environmental, economic, and security-related benefits to our society. Biorefineries provide the option of co-producing high-value, low-volume products for niche markets together with lower-value commodity products, such as industrial platform chemicals, fuels, or energy, which offsets the higher costs that are associated with processing lignocellulosics (Keller 1996, BRDTAC 2002b).

The two technological platforms being explored for the lignocellulose-based biorefinery are complementary. Each technological platform provides different intermediate products for further processing. It is the range of these intermediates that dictates the types of end products that are likely to be successful in a commercial sense.

2.2. Bioconversion platform

Process overview
The bioconversion platform uses biological agents to carry out a structured deconstruction of lignocellulose components. This platform combines process elements of pretreatment with enzymatic hydrolysis to release carbohydrates and lignin from the wood. An overview of the bioconversion platform is provided in Fig. 2-1.

Figure 2-1: Bioconversion platform flowchart (Mabee et al. 2006)
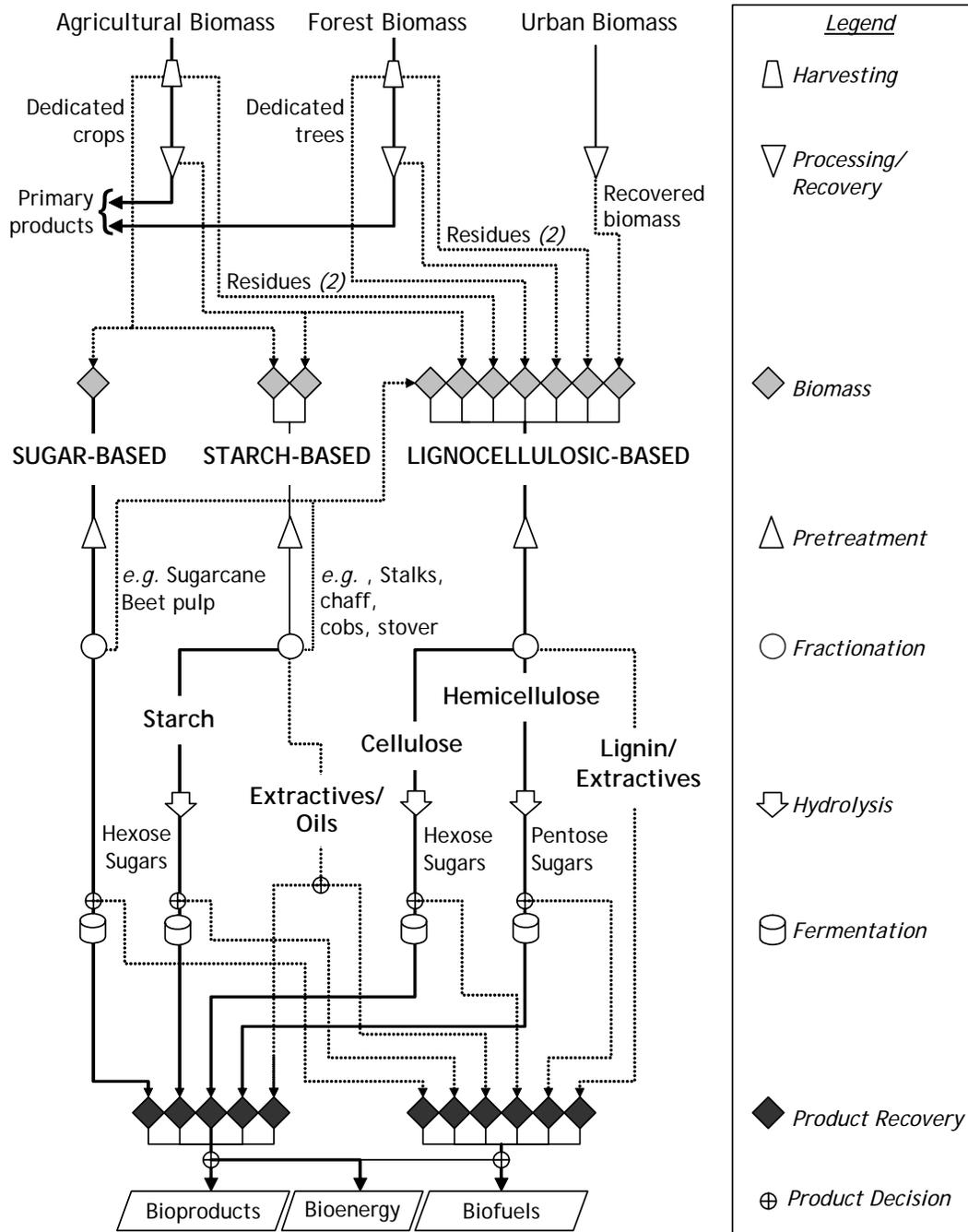
The first step, as shown in the figure, is a pretreatment stage which must optimize the biomass feedstock for further processing. In the bioconversion platform, this step must be designed expose cellulose and hemicellulose for subsequent enzymatic hydrolysis, increasing the surface area of the substrate for enzymatic action to take place. Like in traditional pulping, lignin is either softened or removed, and individual cellulosic fibres are released creating pulp. While bioconversion pretreatment is based on existing pulping processes, however, traditional pulping parameters are defined by resulting paper properties and desired yields, while optimum bioconversion pretreatment is defined by the accessibility of the resulting pulp to enzymatic hydrolysis.

In order to improve the ability of the pretreatment stage to optimize biomass for enzymatic hydrolysis, a number of non-traditional pulping techniques are being examined by a consortium of Canadian and US researchers, including our group at UBC. The Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) has set its objective as advancing the efficacy and knowledge base of pretreatment technologies (Wyman et al. 2005). The pretreatments being considered by the consortia include water-based systems, such as steam-explosion pulping; acidic treatments, using concentrated or dilute acids such as $H2SO4$; alkaline treatments that utilize recirculated ammonia or modified steam-explosion (AFEX); and organic solvent pulping systems, such as acetic acid or ethanol. As with traditional pulping, these pretreatments tend to work best with a homogenous batch of wood chips. Some have observed that different pretreatments seem to be better suited to different types of lignocellulosic feedstocks (e.g. Mabee et al. 2006a).

Once pretreated, the cellulose and hemicellulose components of wood can be hydrolyzed. Almost all commercial hydrolysis programs today use enzymes to facilitate fast, efficient, and economic bioconversion of the wood.   Enzymatic hydrolysis of lignocellulosics uses cellulases most commonly produced by fungi such as Trichoderma, Penicillum, and Aspergillus (Galbe et al. 2002). A cocktail of cellulases is required in order to break down the cellulosic microfibril structure into its carbohydrate components in an efficient manner, unlike the bioconversion of starch, which has a simpler chemical structure. The enzymatic hydrolysis step may be completely separate from the other stages of the bioconversion process, or it may be combined with the fermentation of carbohydrate intermediates to end-products. Separate hydrolysis and fermentation (SHF) offers the platform more flexibility, and makes it easier in theory to alter the process for different end products; however a separate process requires additional engineering and will cost more to build and operate. Simultaneous saccharification and fermentation (SSF) has been found to be highly effective in the production of specific end products, such as bioethanol (Gregg et al. 1998, Galbe et al. 2002, Mabee et al. 2006a)

Separation techniques are being developed to isolate the base components of cellulose, hemicellulose and lignin in order to facilitate industrial processing of these components. Sometimes, the most effective isolation may be carried out by combining correct pretreatments with enzymatic hydrolysis (Mabee et al. 2006a). The strength of the bioconversion platform is that it provides a range of intermediate products, including glucose, galactose, mannose, xylose, and arabinose, which can be relatively easily processed into value-added bioproducts. The bioconversion platform also generates a quantity of lignin or lignin components; depending upon the pretreatment, lignin components may be found in the hydrolysate after enzymatic hydrolysis, or in the wash from the pretreatment stage. The chemical characteristics of the lignin are therefore heavily influenced by the type of pretreatment that is employed. Finally, a relatively small amount of extractives may be retrieved from the process. These extractives are highly variable depending upon the feedstock employed, but may include resins, terpenes, or fatty acids.

Once hydrolyzed, six-carbon sugars can be fermented to ethanol using age-old yeasts and processes. Five-carbon sugars, however, are more difficult to ferment; new yeast strains are being developed that can process these sugars, but issues remain with process efficiency and the length of fermentation. Based on a review of the literature, it is estimated that ethanol yields from lignocellulosics will range between 0.12 and 0.32 L/kg undried feedstock, depending upon

the efficiency of five-carbon sugar conversion. (Gregg et al. 1998, Lawford et al. 1999, 2001, Wingren et al. 2003). Other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream, including lactic acid.

Current status

A large number of technical reports on aspects of bioconversion are available; for examples see Sassner et al. (2005), Berlin et al (2005), and Mabee et al. (2004).   The environmental performance of bioethanol, including air quality (NOx, PM, SOx, etc.) is also well documented; examples include Kemppainen and Shonnard (2005), MacLean and Lave (2003) and Sheehan and Himmel (2001). A number of reports provide mass- and energy- balances of the bioconversion process; for examples see Schulz and Hebecker (2005) and Gravitis et al. (2004). Economic analyses are also plentiful, such as those provided by Wingren et al. (2003) and Rosenberger et al. (2002).

Bioconversion platforms for lignocellulosics-to-ethanol are beginning to become commercially viable. One of the major proponents of bioconversion-to-ethanol is the Iogen Corporation, based in Ottawa. This company has worked since the 1970's to commercialize their proprietary approach, and their demonstration plant has been producing lignocellulose-based ethanol since April 2004 (Iogen 2004). Other major commercial development in this area is being spearheaded by Abengoa Bioenergy, who are constructing a demonstration bioconversion facility at their mill in Salamanca, Spain. This project has Canadian participation from SunOpta Inc., who are providing project engineering and proprietary technology to the project (DOE 2006a).

A number of pilot or process demonstration scale units are also available to support the commercialization process. These include university-based process demonstration facilities in the United States, Canada, Sweden, and Denmark. Pilot-scale faciliti9es include the Etek Etanolteknik pilot facility in Sweden and the National Renewable Energy Laboratory pilot facility in the USA. Abengoa Bioenergy is constructing a pilot facility to explore corn stover-to-ethanol technology at their facility in York, Nebraska (DOE 2006a).

Challenges for commercialization

The most fundamental issues for the bioconversion platform include improving the effectiveness of the pretreatment stage, decreasing the cost of the enzymatic hydrolysis stage, and improving overall process efficiencies by capitalizing on synergies between various process stages. There is also a need to improve process economics by creating coproducts that can add revenue to the process.

Pretreatment research is occurring in a number of laboratories around the world, including Europe, Japan, and North America. As previously mentioned, a number of non-traditional pulping techniques are being examined by a consortium of Canadian and US researchers. The Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) is dedicated to advancing pretreatment technologies, as related to specific feedstocks. In its first round of funding, CAFI members worked with corn stover, while the second round of funding has focused on poplar. The third round of funding, yet to be formally announced, may focus on switchgrass or a perennial lignocellulosic feedstock.

Other fundamental research into the dynamics of bioconversion has lately been focused on the cost of enzymatic hydrolysis, which must be tailored to the complexity of the lignocellulosic matrix. Coordinated projects between Novozymes, Genencor, and the National Renewable Energy Laboratory in the United States succeeded in reducing the cost of enzymatic hydrolysis on ideal substrates by about 30-fold over four years (Novozymes 2005).

Integration of various process steps and increasing overall process efficiency is being improved by integrated research programs, which combine process development units with pilot or demonstration-scale facilities around the world. Process development units are operating at the

University of British Columbia, at Lund University in Sweden, and in the United States at the National Renewable Energy Lab (NREL). Networks of researchers that work at different process scales have combined their efforts to address this issue. It should be pointed out that most of these facilities have been designed to produce bioethanol as their primary product, but can be configured to examine a variety of coproducts.

Bioethanol yields

Based on a review of the literature, it was estimated that ethanol yields from lignocellulosics will range between 0.12 and 0.32 L/kg undried feedstock (Gregg et al. 1998, Wingren et al. 2003, Lawford et al. 1999, 2001). The lowest number represents yields that are currently achievable, while the higher numbers represent potential yields if certain technological issues, including the conversion of pentose sugars, can be achieved. In this report, we consider both the current (low) yield as well as the best yield in order to provide a range of potential 2nd-generation biofuel production.

2.3.   Thermochemical platform

Process overview

This platform uses thermochemical processes to gasify wood, producing synthesis gases (sometimes called producer gases). This platform combines process elements of pretreatment, pyrolysis, gasification, cleanup and conditioning to generate a mixture of hydrogen, carbon monoxide, carbon dioxide, and other gases. The products of this platform may be viewed as intermediate products, which can then be assembled into chemical building blocks and eventually end products (OBP 2003). An overview of the bioconversion platform is provided in Fig. 2-2.

Figure 2-2: Thermochemical platform flowchart (Mabee et al. 2007)
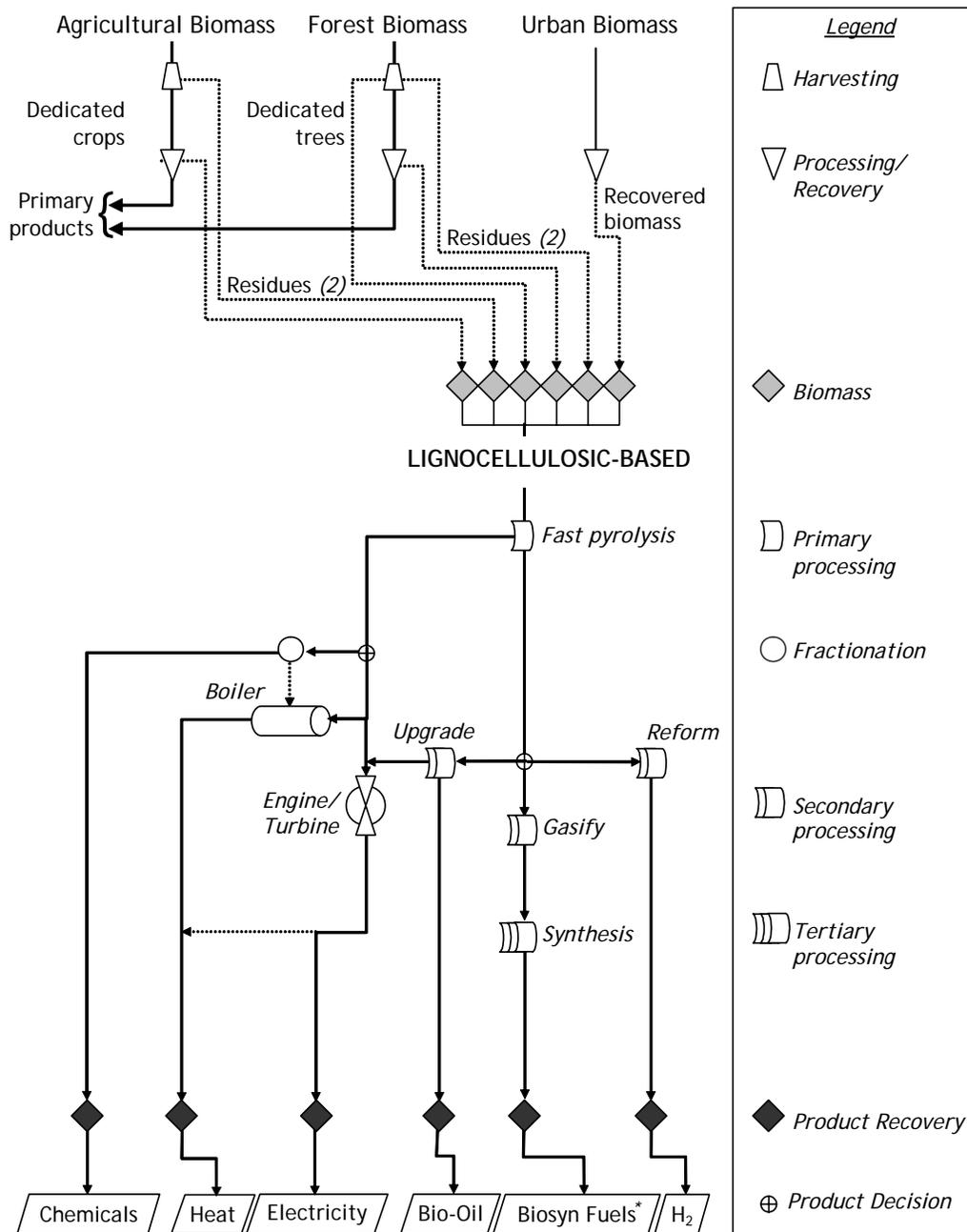
In the thermochemical platform, the only pretreatment required involves drying, grinding, and screening the material in order to create a substrate that can easily be fed into the reaction chamber. The technology required for this stage is already available on a commercial basis, and is often associated with primary or secondary wood processing, or agricultural residue collection and distribution.

In the primary processing stage, the volatile components of biomass are subjected to pyrolysis, or combustion in the absence of oxygen, at temperatures ranging from 450° - 600° C. Depending on how fast the pyrolysis stage is carried out, a variety of products can be achieved. If pyrolysis is carried out quickly (fast pyrolysis), a combination of vapours, condensable vapours, and char is produced.   The condensation of these products creates a bio-oil, which can under ideal conditions make up 60-75% of the original fuel mass. The oil produced can be used as feedstock for value-added chemical products, or possibly as a biofuel (Garcia et al. 2000). If the pyrolysis is carried out at a slower rate (slow pyrolysis), the vapours that are formed are less likely to condense into bio-oil. The vapours themselves consist of carbon monoxide, hydrogen, methane, carbon dioxide and water, as well as volatile tars.

Slow pyrolysis, like fast pyrolysis, leaves behind a solid residue of char (or charcoal), which comprises about 10-25% of the original fuel mass. Processing this material requires a second gasification stage.   Char conversion occurs at temperatures of 700°-1200° C, at which temperatures the char reacts with oxygen in order to produce carbon monoxide (CANMET 2005, Cetin et al. 2005). If the pyrolysis is carried out at the higher temperature range (550° - 600° C), a vapour is formed which consists of carbon monoxide, hydrogen, methane, volatile tars, carbon dioxide and water.   High temperature pyrolysis leaves behind a solid residue of char (or charcoal), which makes up about 10-25% of the original fuel mass. This material can then be gasified at temperatures of 700°-1200° C, and used as a fuel source to drive the pyrolysis process (Cetin et al. 2005). All gaseous products from pyrolysis and gasification are generally referred to as synthesis gases (or syngas).

After the production of syngas, a number of pathways may be followed to create 2nd-generation biofuels or other chemical, heat, or energy products, as shown in Fig. 2-3. It is possible to create one potential biofuel from the thermochemical platform without a catalysis stage. Bio-oil has been advocated as a substitute for bunker-grade heating oil, and is approved for use in district heating utility boilers in Sweden. It has been mixed with coal in a co-firing facility in the United States successfully.   The CANMET Energy Technology Centre is exploring a micro emulsion process that allows bio-oil to be mixed with conventional diesel engines.   Other biofuels may be generated by applying a catalysis stage. The truly 'revolutionary' aspect of the thermochemical platform is its ability to use this approach to convert syngas into chemical building blocks and eventually end products.   Proven catalytic processes for syngas conversion to fuels and chemicals exist using syngas produced commercially from natural gas and coal. These proven conversion technologies can be applied to biomass-derived syngas.

Methanol is one potential biofuel that can be generated through catalysis.   The majority of methanol produced today is being derived from natural gas, however. Methanol has a high octane number (129) but relatively low energy (about 14.6 MJ/l) compared to gasoline (91-98 octane, 35 MJ/l).   Methanol is mostly used to create MTBE, which is used as an octane booster today. Conceivably, methane could be used in higher or as a stand alone fuel, although this would require significant infrastructure changes as well as modifications to conventional engines. Because methanol has a favourable hydrogen:carbon ratio (4:1), it is often touted as a potential hydrogen source for future transportation systems.

Another potential biofuel that can be produced through the thermochemical platform is Fischer-Tropsch diesel (or biosyn diesel). This fuel was first discovered in 1923 and is commercially based on syngas made from coal, although the process could be applied to biomass-derived syngas. The process of converting CO and H2 mixtures to liquid hydrocarbons over a transition metal catalyst has become known as the Fischer-Tropsch (FT) synthesis.   Most existing production of FT-diesel was carried out in South Africa, in part because that country was under

UN trade sanctions for many years and had no available source of petroleum for fuel production. Eventually, five plants were built in South Africa in the 1980's and 1990's (three based on coal, and one based on natural gas); and a number of other natural gas-based plants have been commissioned or constructed around the world in the late 1990's.

Another potential catalytic conversion of biomass-based syngas is to higher alcohols, including ethanol. Ethanol and other higher alcohols form as by-products of both Fischer-Tropsch and methanol synthesis, and modified catalysts have been shown to provide better yields. The thermochemical platform provides the opportunity for a number of additional coproducts, as well as energy in the form of heat or electricity and biofuels. Each syngas component (i.e. CO, CO_2, CH_4, H_2) may be recovered, separated, and utilized.

Current status

Pyrolysis/gasification systems have been reported to be much more efficient for energy recovery, in terms of electricity generation, than traditional combustion. It has been estimated that typical biomass steam generation plants have efficiencies in the low 20% range, compared to gasification systems with efficiencies that reach 60% (DOE 2006b). High efficiencies have been noted for both co-firing systems (where biomass is gasified together with a fossil fuel such as coal or natural gas) and in dedicated biomass gasification processes (Gielen et al. 2001). Because the potential for energy recovery is so much higher, gasification systems without any downstream catalysis may be able to increase bioenergy production with minimal impact on existing product streams in sawmilling or pulping operations. This type of 'evolutionary' technology application is a logical step on the path towards greater process efficiencies and increased energy self-generation. These types of systems could also provide surplus bioenergy, becoming an additional revenue stream and diversifying the economic portfolio of the Canadian forest industry.

In terms of 2nd-generation biofuel production, the majority of the literature focuses on a platform that links gasification technology to the Fischer-Tropsch synthesis process. From an environmental perspective, a number of studies are available that examine emissions associated with this fuel's use; for examples see Szybist et al. (2005) and Kahandawala et al. (2004). The economic and energy costs associated with these fuels use are addressed by a number of authors; for examples refer to Prins et al. (2005), who supply an exergy analysis of a combined gasification-Fischer-Tropsch synthesis system, and Hamelinck et al. (2004), who provide a mass/energy balance for biomass-based FT diesel systems, as well as an overview of costs and returns. Refining, blending and commercialization issues have also been addressed in the literature; see Tijmensen et al. (2002) for an example. Significant technical hurdles remain in the creation of 2nd-generation biofuels through the thermochemical platform, including syngas clean-up, char accumulation, and catalysis inhibition.

While thermochemical-derived 2nd-generation biofuels are not yet technically proven, there are a number of pilot- and demonstration-scale pyrolysis or gasification facilities capable of processing biomass. These include government-run facilities in the CANMET Energy Technology Centre in Ottawa, as well as the Thermochemical Users Facility at the National Renewable Energy Lab in the United States. Canada is also home to a number of commercial ventures, including Ensyn, Enerkem, Dynamotive, and Nexterra. At the present time, most of these facilities are focused on creation of bioenergy (including Nexterra and Dynamotive), generating bio-oil (Dynamotive), or creating value-added components from the volatile tar components (Ensyn and Enerkem). In the United States, a number of commercial initiatives include projects led by Georgia Pacific, Boise Cascade, and Mississippi Ethanol LLC (DOE 2006c,d,e,f). At the present time, there are no commercial-scale biomass-based facilities for the production of fuels or chemicals using the thermochemical platform (Faaij 2006).

Challenges for commercialization

Gasification technologies for the production of fuels from biomass has been tested in Europe, but has failed to attract interest in the past due to the comparatively low price of fossil fuels (Faaij 2006). This is changing with rising fuel costs and uncertainty about the security of fossil reserves.

Part of the problem with commercializing thermochemical fuels may be related back to the quality of bio-based synthesis gases, which are more heterogeneous than natural gas-based syngas. While technical approaches are well documented for the production of hydrogen, methanol and FT liquids from syngas, the input gases must be relatively clean in order for these processes to function in a commercially viable sense.   Therefore, before catalysis, raw syngas must be cleaned up in order to remove inhibitory substances that would inactivate the catalyst. These include sulphur, nitrogen, and chlorine compounds, as well as any remaining volatile tars. The clean-up of heterogeneous biomass-derived syngas is one of the primary technical issues that remains to be addressed.

The ratio of hydrogen to carbon monoxide may need to be adjusted and the carbon dioxide by-product may also need to be removed. One major problem with methanol synthesis is that biomass-based syngas tends to be hydrogen-poor compared to natural gas syngas. Methanol synthesis requires a ratio of 2:1 hydrogen:carbon monoxide to be cost-effective. Research is ongoing to allow lower ratio hydrogen:carbon monoxide syngas to be used.   Again, this is a key issue in generating a value-added chemical component that could support biorefining operations.

Common problems associated particularly with Fisher-Tropsch synthesis are low product selectivity (the unavoidable production of perhaps unwanted coproducts, including olefins, paraffins, and oxygenated products), and the sensitivity of the catalyst to contamination in the syngas that inhibit the catalytic reaction. With biomass-based syngas, this problem is amplified due to the heterogeneous nature of the syngas. Research to improve the ability of catalysts to resist inhibitors is required to lower the cost of production to economic ranges.

A final issue, perhaps of greater concern to policymakers, is that deployment on a large scale is required to gain necessary economies of scale for most of these processes, where the cost of syngas production can easily be more than 50% of the total process cost (Spath and Dayton 2003).   This means larger plants and ultimately fewer employees on a per-litre basis of fuel output. This requirement for large facilities raises the level of capital required for infrastructure development, increasing risk to the investor; it also increases the amount of biomass required for operation, which makes it more difficult to supply the facility over the course of its operational lifetime.

Biofuel yields
A review of data reported in Spath and Dayton (2003) shows that potential yields for Fischer-Tropsch fuels are between 0.075 and 0.2 L/kg per wet tonne of lignocellulosic biomass. Ethanol from thermochemical sources, as yet untested, could potentially be generated in the range of 0.145 L/kg feedstock.   While fuels from thermochemical sources are not yet near commercialization, we considered the upper and lower bounds for F-T fuels in the same way that we considered figures for bioconversion.

2.4.   Greenhouse gas production

Greenhouse gas production associated with lignocellulosic-based feedstocks is anticipated to be much lower than with conventional fuels. The environmental performance depends very much on the specific life cycle of the fuel, including the country in which the life cycle assessment (LCA) was conducted, the feedstock on which the fuel is based, the vehicle used, the propulsion system, and the overall state of technology. Two major integrative reports have been carried out that have brought together the major LCA's conducted in a number of OECD countries in Europe and North America. One, the VIEWLS project, released their first report in November of 2005 (VIEWLS 2005). An earlier report by the Institute for Energy and Environmental Research in Heidelberg corroborates many of the findings in the VIEWLS report and provides some additional LCA reviews (Quirin et al. 2004).

In general, both reports show that fuels (and chemicals) made from lignocellulosic materials are characterized by reduced carbon dioxide emissions when compared to similar products derived from petroleum and thus can play a role in meeting Kyoto Protocol obligations or reduced pollution guidelines.   Conventional fuels have emissions ranging between 160 to 190 g CO_2-equivalent per kilometre; most biofuels, including the 2nd-generation fuels we are discussing in this report, can reduce these significantly. It is pointed out that substituting emissions by utilizing bio-based energy in all aspects of 2nd-generation biofuel production can create an overall negative emission for the fuel (VIEWLS 2005, Braune 1998). For the purpose of this report, we do not consider this potential, but rather simply focus on the potential of 2nd-generation biofuels to reduce GHG emissions in use.

Fig. 2-3 on the next page illustrates the dramatically lower GHG emissions that are associated with 2nd-generation biofuel use. It is found that Fischer-Tropsch (F-T) fuels based on residues are likely to have the lowest possible emissions; this is typical of diesel propulsion systems that have better energy recovery. If energy crops are utilized as a feedstock, the overall emissions rise slightly, because the benefit of residue disposal is lost. Ethanol from residues or from energy crops also have relatively low emissions, particularly compared to conventional fuels including gasoline and diesel fuel.

For 2nd-generation ethanol from lignocellulosics, there is a potential to reduce GHG emissions with improved technology, which may be available post-2010. This reflects the close-to-commercial status of the technology today, and the anticipated improvements that will be seen as this technology improves. For F-T fuels, it is anticipated that commercial status will not be achieved until post-2010, reflecting the significant technical hurdles which must be met with this technology platform. There is also a potential to reduce emissions associated with gasoline and diesel production and use, which is reflected in the '>2010' figures below.

Figure 2-3: GHG emissions associated with 2nd-generation biofuels (g CO2-e/km)
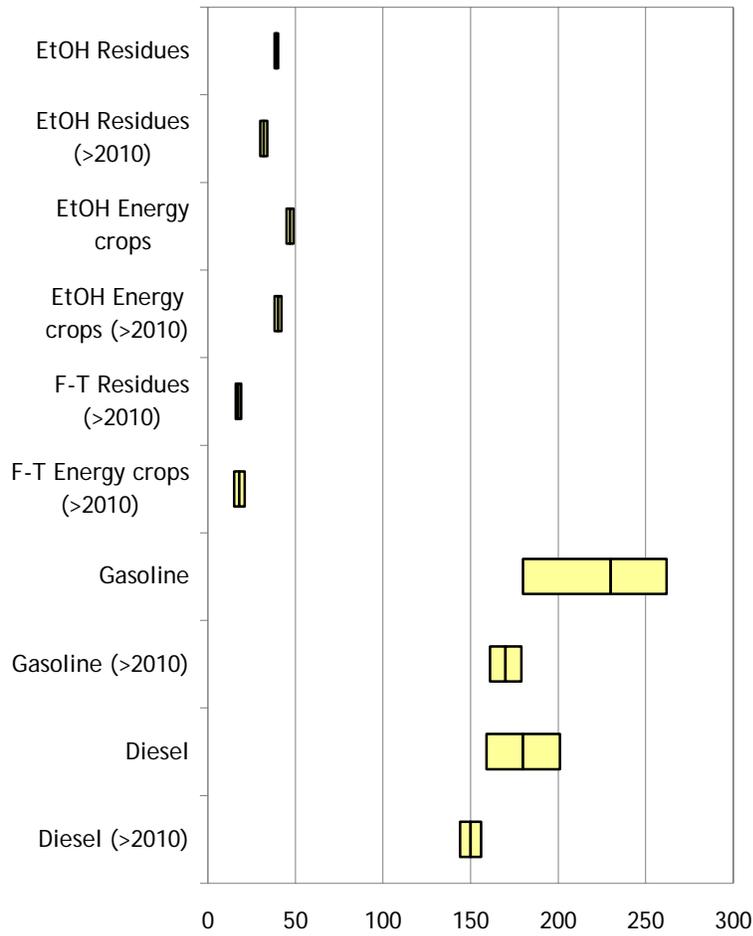
3.   Coproduct Generation

3.1.   Major coproducts associated with thermochemical conversion

One of the major implications of thermochemical-based scenarios is the ability to generate excess heat and power.

Bioenergy is a defining component of a biorefinery. Self-generation of heat and power by the combustion of a portion of biomass feedstock can offset fossil fuel requirements, displacing the load on utilities and improve the environmental performance of the facility. The forest products industry has typically viewed energy projects with some trepidation, as investment in energy production would take away from the core business of pulp, paper or wood product manufacture. Because of this, the industry demands a much higher internal rate of return on their energy-related investments than do electrical utilities. However, the cost of buying natural gas to generate heat and power internally has risen dramatically. In June 1996, the cost of natural gas was about $1/GJ (CDN currency), but by 2005, the average price has risen to about $7/GJ (NRCan 2005a). Electricity costs have risen as well, increasing self-generation as a viable alternative.

In the pulp and paper industry, today's Kraft pulp mills effectively use biomass residues contained in black liquor to generate heat and power through recovery boilers; biomass is estimated to contribute more than 50% of total fuel use by the pulp and paper industry in both the US and in Sweden (Farahani et al. 2004). The evolution of pulp mills towards biorefining might include upgrading recovery boilers with thermochemical technologies under development, including fast pyrolysis and gasification (BRDTAC 2002a). Other options for improved energy production include co-firing or cogeneration (i.e. combining biomass with fossil fuels in combustion). It is estimated that gasification technology has the potential to generate approximately twice as much electricity per ton of black liquor as a conventional recovery boiler (Farahani et al. 2004, Larson et al. 2000). This additional power can reduce the need to purchase natural gas, coal, oil and electricity for everyday operations, increasing the economic performance of the facility.

The rising cost of energy today has increased the impetus for the pulp and paper industry to move towards 100% self-generation of power. It has been estimated that one tonne of softwood lignin embodies between 22.2-23.5 GJ of energy (LHV/HHV) (ECN 2005). This means that one dry tonne of lignin can be worth approximately ($7*22.2) or $155/tonne in energy value to a mill that currently utilizes natural gas, up from $22/tonne in 1996. Using standard net heating value for wood (Dietenberger 2002), it can be estimated that at 50% moisture the value of lignin remains high, at about $140/tonne.   At this value, self-generation of heat and power for in-mill use may be economical, even given the predilection of the wood products industry to view energy projects as outside their mandate. There is some government support for investment in more efficient self-generation technology. For example, the Renewable Energy Deployment Initiative (REDI), introduced by Natural Resources Canada in 1998, can be used to offset 25% of purchase and installation costs of biomass energy systems, up to a total of $80,000 (CDN) per installation (Bernotat and Sandberg 2004).

Excess heat and power can be utilized for additional value-added processing, or can be distributed through a local network to provide district heating of nearby businesses and residences (NRCan 2006). The potential appeal of bioenergy as a product may be limited, however, by the regulatory regime which governs electricity generation, transmission, and sales. Two Canadian provinces, Alberta and Ontario, have been considering deregulation of the electricity industry, but the negative experiences that some US jurisdictions have had with deregulation (notably California) may reduce the willingness of Canadian consumers to embrace a deregulated market. In Canadian markets today, energy generators are limited to wholesale transmission access, or wholesale 'wheeling', which allows them to sell energy to a utility. To do so, the generator must enter into purchase agreements with the utilities that provide power to consumers. For instance, the largest bioenergy generation facility in Canada, the Williams Lake

Cogeneration facility run by Terasen, has a 20-year purchase agreement with BC Hydro. Typically, each agreement is negotiated individually. Green power incentives, such as the recently introduced Renewable Power Production Incentive (RPPI), will pay an incentive of 1¢ per kilowatt-hour of production for the first ten year of operation for eligible projects, which include biomass projects (NRCan 2005b).

3.2.   Major coproducts associated with bioconversion

One of the major implications of bioconversion is its ability to support a number of value-added coproducts.

In the past, chemical products were a major part of the forest industry. A number of chemical forest products, based on extractives, were the basis of a thriving industry in North America from the early 1700's to the onset of World War II in 1939. These products included pitch (partially dried resins), pine tar (liquefied resins), turpentine (terpenes from distilled resins), rosin (the involatile residues from resin distillation). Later, tall oils (which were obtained from alkaline pulping liquors) added the naval stores category; tall oils could be fractionated into tall oil rosin and tall oil fatty acids. These products were widely used in wooden shipbuilding & operation, which lent this product category its name of 'Naval stores.' Today, a limited amount of forest-based naval stores are still produced and used to manufacture soap, paper, paint, and varnishes. While few up-to-date estimates of this industry exist, a review was carried out in the mid-1990's by the Food and Agriculture Organization of the United Nations (Coppen and Hone 1995). It was reported that about 1.2 million tonnes of rosin worth approximately $400 million (US currency) was produced in 1995, a third of which was tall oil rosin based on sulphite liquor. In the same year, about 330,000 tonnes of turpentine was produced, totalling about $50 million; two-thirds of this amount was turpentine recovered during Kraft pulping. The major producers of forest-based naval stores included China, India, Russia, Brazil, and Portugal at the time of the report (Coppen and Hone 1995).

Today, there is a resurgence of interest in renewable biochemicals as a means of reducing our reliance upon petroleum-based products. Research has shown that a number of the platform chemicals that supply advanced manufacturing may be generated from biological sources (Spath et al. 2003, Werpy et al. 2004). The chemical products that can be derived from the biorefinery have the potential to become a significant part of Canada's economy in the future. The potential Canadian market for industrial chemical bioproducts has been estimated at about $1.7 billion/year (Canadian currency) (Crawford 2001, CANUC 2002). Health-related chemicals, which can include nutraceuticals, essential oils, pharmaceuticals, drugs, and medicines, have a potential Canadian market of $260 million/year. Finally, niche products designed for bioremediation and phytoremediation of contaminated soils, as well as biocontrols designed to contain and control chemical spills, have a Canadian market anticipated to be $50 million/year (Crawford 2001). In the United States, where biorefining efforts based on agricultural biomass are relatively advanced, significant work has been done by the Biomass Research and Development Technical Advisory Committee to define goals for bioproducts. These goals included tripling the amount of bioproducts consumed by 2010, providing benefits to farmers and forest landowners by increasing the value of agricultural and forest biomass, and reducing the environmental impacts of consumer goods through substitution and increased use of bioproducts (BRDTAC 2002a).

Biochemical development in the United States is largely based on sugars. As discussed earlier, sugars are one of the main intermediate products of the bioconversion platform. The report entitled 'Top value Added Chemicals from Biomass', produced by the Pacific Northwest National Laboratory and the National Renewable Energy Lab, identified candidate products, and specified if the necessary technology pathways were under development or commercially available (Werpy et al. 2004). A range of products, including sorbitol, furfural, itaconic acid, glutamic acid, xylitol/arabitol, and glycerol, are already produced commercially. A forest-based biorefinery based on the bioconversion platform could provide inexpensive sugars as feedstocks to these processes.

One of the emerging commercial opportunities for sugar-based biochemicals is in the area of bulk polymers. In the US, there are two major projects underway to produce bulk biopolymers, for use in textiles and packaging applications. One of these was launched by Cargill under the name Natureworks LLC, which produces two polymer products derived from polylactide (PLA). Polylactide is derived from lactic acid, which is generated from sugars through bacteria fermentation. The commercial products based on this polymer include Natureworks PLA, bulk packaging for the food and beverage sector, and Ingeo Fibre, a textile product that can be used in apparel and other applications [50]. While these products are currently based on sugars derived from corn starch, the company is working with Genencor International and Iogen to expand their feedstock to lignocellulosics (DOE 2006g). A second major project has been undertaken by E.I. DuPont de Nemours & Co., in partnership with the Diversa Corporation. This consortium is developing processes to transform corn stover, a lignocellulosic feedstock, into glucose and then into 3-hydroxypropionic acid (3-HPA), which can be reduced into 1,3-propanediol (DOE 2006h). This is being processed into a polymer fibre by DuPont and marketed as Sorona Fibre. 3-HPA can also be dehydrated to produce a variety of acrylic products, including acrylic acid and acrylamide, which can then be used in products such as diapers. This polymer has unique properties, such as stretch recovery, resiliency, toughness, and easy dye capability. It can be manufactured in existing facilities. Cargill is also working on pathways to generate 3-HPA, in conjunction with Codexis and the US DOE (DOE 2006i).

Another area currently seeing development is the production of 1,4-diacids. For example, Bolak and Company are working on a US DOE-funded project to demonstrate the production of succinic acid in an ethanol dry mill, using ammonia fibre explosion (AFEX) pretreatment to process corn fibre and eventually switchgrass (DOE 2006i). The 1,4-diacids act as a precursor in many industrial processes, and could replace the benzene class of commodity petrochemicals. It can be used in the manufacture of butanediol, tetrahydrofuran, and pyrolidinones, chemicals with application in plastics, paints, and inks. Other interesting derivatives of this product include lactate acid and ascorbic acid (vitamin C), which can be used in a variety of food products.

Monomers generated by the bioconversion platform may be converted through chemical means into levulinic acid (LA). This chemical is used as a building block in the manufacture of industrial products. Partial reduction of levulinic acid can lead to a fuel additive known as LA-methyltetrahydrofuran (MTHF), which could potentially have a large market in traditional or biofuels. Complete reduction of LA leads to 1,4-pentanediol, which could form the basis of new biopolyesters. Through oxidation, acetyl acrylates may be generated, which may be used to enhance the properties of other monomers. LA may also be converted into a herbicide known as delta-amino levulinic acid, which has a market of $US 0.4-0.9 billion per year (Werpy et al. 2004, Crawford 2001). This bioproduct is well on its way to commercialization, with a 1-ton per day pilot plant constructed in New York State by the Biofine Corporation, in conjunction with NREL, PNNL, New York State, and Chemical Industry Services.

4.   Conclusions

There are three separate yet complementary approaches to developing the forest-based biorefinery: (1) re-engineer existing pulp and paper or sawmill operations to create biofuels, biochemicals, or bioenergy as a coproduct to the traditional forest product; (2) re-engineer existing facilities, or develop new operations that can maximize bioenergy recovery, and develop downstream processing to generate biofuels or biochemicals; or (3) develop greenfield operations capable of delivering intermediate chemical products that may be further processed into biofuels, platform chemicals and bulk polymer applications, and bioenergy.

The first approach, adapting a modern pulp mill to act as a biorefinery, means utilizing a portion of mill feedstocks for alternative products, but also implies that the focus will remain on traditional forest products. Modern pulp mills are highly efficient and leave behind few residues that can easily be directed into biorefining operations.   Perhaps the most obvious adaptation is the introduction of thermochemical platform elements to the Kraft pulping process for improved energy recovery from black liquor. Bioconversion process elements might be included as a pretreatment to the pulping process itself, where easily hydrolysable sugars are stripped away from the pulp in order to create a parallel feedstock to the traditional pulping technology, and perhaps improve the quality of the paper being produced. In older pulp and paper mills built on sulphite pulping technology, the absence of efficient liquor recycling provides an easily accessed feedstock for biorefining. In Canada, the Tembec facility in Temiscaming is an excellent example of the biorefinery concept being applied to an older facility. The problem with this type of approach is that process efficiency will be sacrificed, and the feedstock diverted to secondary products will not be optimal but instead will consist of residual, heterogeneous materials.

The second and third approaches may be differentiated from the first by the decision to make biofuels a dominant output of the biorefinery rather than a coproduct. These approaches consider the long-term evolution of pulping facilities towards more diverse biorefineries that are capable of producing energy, fuels, and chemicals, as well as a variety of material products.

In the United States and Canada, the bioconversion platform remains dominant today. A great deal of effort has focused on the production of ethanol from sugars, which may be derived from lignocellulose through the bioconversion platform. Since 1976, over 80 new ethanol production facilities have been built in the U.S. primarily using starch as a feedstock. The overwhelming majority of proponents in North American biofuel production have demonstrated expertise in the biological pathways of hydrolysis and fermentation. This availability of expertise is an important element of commercial success.

The bioconversion platform is rapidly approaching commercial deployment in the agricultural sector and has achieved demonstration status for lignocellulosics. An economical technology for bioconversion of lignocellulosic biomass would greatly extend the potential of the ethanol industry to become a substantial contributor to the fuel and energy requirements of Canada. The great advantage of the bioconversion platform is that it offers a means to generate sugars from lignocellulosics, which can act as feedstocks for a number of new biochemical products being commercialized today. A number of processes currently being demonstrated for different bioproduct generation in the United States could give this platform the ability to generate bulk polymers, textiles, food packaging, and nutraceuticals. This represents a radical departure from traditional forest products and brings a number of marketing and production challenges. Finally, the scale of operations for bioconversion facilities is closer to the typical size of a forest products mill, and provides an advantage for potential employment.

It is estimated that bioethanol from the bioconversion platform has the ability to offset a greater amount of greenhouse gas emissions than does thermochemical-derived fuels, but this is due to the nature of the conventional fuel that is being replaced, and the energy content of the biofuel. The percentage reduction in emissions associated with biosyn diesel is lower when compared to bioconversion-based ethanol. This is because ethanol is seen to replace gasoline, which in turn

has higher inherent emissions. In terms of net greenhouse gas emissions, thermochemical-derived fuels have an advantage.

Major technical issues remain for the thermochemical production of 2nd-generation biofuels, including the quality of syngas, the accumulation of char, and inhibition of the catalysis stage. If these technical issues can be overcome, our models show that the widespread uptake of biosyn diesel could provide the greatest total GHG savings of all 2nd-generation biofuels. Because biosyn diesel would likely be offered as a blend with traditional diesel, this scenario relies upon increased traditional diesel use, which is more likely to occur in Europe than in North America. A number of preliminary steps would be required, including revisiting existing taxation on traditional fuels. In terms of coproducts, the thermochemical platform is currently most effective at delivering energy, which may reduce operating costs for a mill significantly, but as a product may not offer high returns to the company in a regulated energy market. Finally, the potential for direct employment with the thermochemical platform may be smaller than with bioconversion, because of the likely need for large scale operations that can achieve process efficiencies.

An opportunity exists to implement policy that supports lignocellulosic-based biorefining efforts, regardless of platform. In particular, national policy should be designed to complement provincial approaches, and to support biorefining initiatives using both technological platforms. There are many positive reasons to create this type of policy. Biorefineries based on lignocellulosics will be able to access a much wider variety of feedstocks, including forest biomass. Successfully doing so will increase security of supply and improve the ability of biorefineries to support a transition to a carbohydrate-based economy. The dependence of bioproducts upon specific feedstocks becomes less significant as the complexity of the process increases; thus, biorefineries that rely upon lignocellulosic material can utilize a more diverse selection of biomass. It is clear that no single biomass option can source the total demand for fuels and chemicals, and that different feedstocks and technologies will require significantly different policy approaches.

5.   Literature Cited

1.   Atchison, J.E. (1993). In Pulp and Paper Manufacture Vol. 3, Secondary Fibers and Non-Wood Pulping, Hamilton, F., Leopold, B., and Kocurek, M.J., eds., TAPPI, Atlanta, pp. 4-16.

2.   Berlin, A., Gilkes, N., Kurabi, A., Bura, R., Tu, M., Kilburn, D. and Saddler, J.N. (2005). Weak lignin-binding enzymes - A novel approach to improve activity of cellulases for hydrolysis of lignocellulosics. Appl. Biochem. Biotechnol. 121: 163-170.

3.   Bernotat, K. and Sandberg, T. (2004). Biomass fired small-scale CHP in Sweden and the Baltic States: a case study on the potential of clustered dwellings. Biomass Bioenergy 27(6): 521-530.

4.   Bowyer, J.L. and Stockmann, V.E. (2001). Agricultural residues - An exciting bio-based raw material for the global panels industry. For. Prod. J. 51(1): 10-21.

5.   Braune, I. (1998). The contribution of agriculture and forestry to climate protection - agriculture and forestry policy in Germany. Berichte Uber Landwirtschaft 76(4), 580-597.

6.   BRDTAC. (2002a). Roadmap for biomass technologies in the United States. Biomass Research and Development Technical Advisory Committee, Washington, DC.

7.   BRDTAC. (2002b). Vision for bioenergy and bio-based products in the United States. Washington, DC: Biomass Research and Development Technical Advisory Committee.

8.   CANUC. (2002). Non-Food/Non-Feed Industrial Uses for Agricultural Products: Phase 1. Ottawa, ON: Agriculture and Agri-Food Canada, Canadian New Uses Council, 84 pp.

9.   CANMET. (2005). Gasification Research. Ottawa, ON: CANMET Energy Technology Centre. http://www.nrcan.gc.ca/es/etb/cetc/cetc01/htmldocs/factsheet_gasification_research_e.html. Last accessed Dec. 28/05.

10.   Cao, C., Wang, Y., Hu, J., Elliot, D., Jones, S., and Stevens, D. (2003). Microchannel catalytic process for converting biomass derived syngas to transportation fuels. Battelle/Pacific Northwest National Laboratory: Presentation to the ACS, New York, NY, Sept. 8 2003.

11.   CCFM (2003). Compendium of Canadian Forestry Statistics, Canadian Council of Forest Ministers, Ottawa, ON.

12.   Cetin, E., Moghtaderi, B., Gupta, R. and Wall, T.F. (2005). Biomass gasification kinetics: Influences of pressure and char structure. Combustion Sci. Technol. 177(4): 765-791.

13.   Coppen, J.J.W. and Hone, G.A. (1995). Gum naval stores: Turpentine and rosin from pine resin. Rome, Italy: Food and Agriculture Organization of the United Nations, 62 pp.

14.   Crawford, C. and Canadian New Uses Council (CANUC). (2001). Discussion Framework: Developing Biobased Industries in Canada. Ottawa, ON: Agriculture and Agri-Food Canada, 69 pp.

15.   Dietenberger, M. (2002). Update for combustion properties of wood components. Fire Mater. 26: 255-267.

16.   DOE. (2006a). Advanced biorefining of distiller's grain and corn stover blends. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/advanced_biorefining.pdf. Last accessed Jan. 02/06.

17.   DOE. (2006b). Electricity from biomass. Washington, DC: US Department of Energy; http://eereweb.ee.doe.gov/biomass/electrical_power.html. Last accessed Jan. 02/06.

18.   DOE. (2006c). DOE Thermochemical Users Facility. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/33817.pdf. Last accessed Jan. 02/06.

19.   DOE. (2006d). Big Island Demonstration Project - Black Liquor. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/big_island_black_liquor.pdf. Last accessed Jan. 02/06.

20.   DOE. (2006e). Gasification-based fuel conversion and electricity production in the forest products industry. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/gasification_based_fuel_conversion.pdf. Last accessed Jan. 02/06.

21.   DOE. (2006f). Mississippi Ethanol gasification project. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/mississippi_ethanol_gasification.pdf. Last accessed Jan. 02/06.

22.   DOE. (2006g). Making industrial biorefining happen! Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/making_industrial_biorefinery.pdf. Last accessed Jan. 02/06.

23.   DOE. (2006h). Integrated corn-based bio-refinery. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/integrated_cornbased_biorefinery.pdf. Last accessed Jan. 02/06.

24.   DOE. (2006i). New platform intermediates. Washington, DC: US Department of Energy, Office of Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/biomass/pdfs/factsheets/fy04/new_platform_intermediates.pdf. Last accessed Jan. 02/06.

25.   ECN. (2005). Phyllis, database for biomass and waste. Petten, NL: Energy Research Centre of the Netherlands (ECN). http://www.ecn.nl/phyllis/DataTable.asp. Last accessed Dec. 21/05.

26.   Economagic. (2006). West Texas intermediate crude oil prices, dollars per barrel. www.economagic.com. Last accessed Mar. 30/06.

27.   Environment Canada. (1992). Agricultural land use change in Canada. Ottawa, ON: Environment Canada.

28.   FAO. (2006a). FAOStat Agriculture Data. Rome, Italy: Food and Agriculture Organization of the United Nations. Available online at www.faostat.org. Last accessed March 12, 2006.

29.   FAO. (2006b). FAOStat Forestry Data. Rome, Italy: Food and Agriculture Organization of the United Nations. Available online at www.faostat.org. Last accessed March 12, 2006.

30.   FAO. (2005). State of the World's Forests. Rome, Italy: Food and Agriculture Organization of the United Nations.

31.   Faaij, A.P.C. (2006). Bio-energy in Europe: changing technology choices. Energy Policy 34(3): 322-342.

32.   Farahani, S., Worrell, E., and Bryntse, G. (2004). CO2-free paper? Resources, Conservation and Recycling 42(4): 317-336.

33.   Galbe, M. and Zacchi, G. (2002). A review of the production of ethanol from softwood. Appl. Microbiol. Biotechnol. 59(6): 618-628.

34.   Garcia, L., French, R., Czernik, S. and Chornet, E. (2000). Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. Applied Catalysis A: General 201(2): 225-239.

35.   Gielen, D.J., de Feber, M.A., Bos, A.J. and Gerlagh, T. (2001). Biomass for energy or materials? A Western European systems engineering perspective. Energy Policy 29(4): 291-302.

36.   Gravitis, J., Zandersons, J., Verdernikov, N., Kruma, I., and Ozols-Kalnins, V. (2004). Clustering of bio-products technologies for zero emissions and eco-efficiency. Ind. Crops Prod. 20(2): 169-180.

37.   Gregg, D.J., Boussaid, A. and Saddler, J.N. (1998). Techno-economic evaluations of a generic wood-to-ethanol process: Effect of increased cellulose yields and enzyme recycle. Bioresource Technology 63(1): 7-12.

38.   Hamelinck, C.N., Faaij, A.P.C., den Uil H., and Boerrigter, H. (2004). Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential. Energy 29(11): 1743-1771.

39.   IEA (2003). Renewables Information 2003. IEA Statistics. Paris, France, International Energy Agency.

40.   Iogen. (2004). Cellulose ethanol is ready to go. Press Release, 21 April 2004.

41.   IPCC. (2000). Special report on emissions scenarios. Cambridge, UK: Intergovernmental Panel on Climate Change.

42.   Kahandawala, M.S., Graham, J.L. and Sidhu, S.S. (2004). Particulate emission from combustion of diesel and Fischer-Tropsch fuels: A shock tube study. Energy & Fuels 18(2): 289-295.

43.   Keller, F.A. (1996). Integrated bioprocess development for bioethanol production. In Handbook on Bioethanol: Production and Utilization. Wyman, C.E., ed. Washington, DC: Taylor & Francis, pp. 351-379.

44.   Kemppainen, A.J. and Shonnard, D.R. (2005). Comparative life-cycle assessments for biomass-to-ethanol production from different regional feedstocks. Biotechnol. Prog. 21(4): 1075-1084.

45.   Larson, E.D., McDonald, G.W., Yang, W., Fredrick, W.M.J., Iisa, K., Kreutz, T.G., Malcolm, E.W. and Brown, C.A. (2000). A cost-benefit assessment of BLGCC technology. Tappi J. 83(6): 1–16.

46.   Lawford, H.G., Rousseau, J.D. and Tolan, J.S. (2001). Comparative ethanol productivities of different Zymomonas recombinants fermenting oat hull hydrolysate. Applied Biochemistry and Biotechnology 91-93: 133-146.

47.   Lawford, H.G., Rousseau, J.D., Mohagheghi, A., and McMillan, J.D. (1999). Fermentation performance characteristics of a prehydrolyzate-adapted xylose-fermenting recombinant Zymomonas in batch and continuous fermentations. Applied Biochemistry and Biotechnology 77-79: 191-204.

48.   Lindstrom, M., Skidmore, E., Gupta, S., and Onstad, C. (1979). Soil conservation limitations on removal of crop residues for energy production. Journal of Environmental Quality 8(4): 533-537.

49.   Lynd, L.R., Wyman, C.E., and Gerngross, T.U. (1999). Biocommodity engineering. Biotechnol. Prog. 15(5): 777-793.

50.   Mabee, W. E., Gregg, D. J., Arato, C., Berlin, A., Bura, R., Gilkes, N., Mirochnik, O., Pan, X., Pye, E. K. and Saddler, J. N. (2006a). Update on softwood-to-ethanol process development. Appl. Biochem. Biotechnol. (in press).

51.   Mabee, W.E., Gregg, D.J., and Saddler, J.N. (2006b). Canadian biomass reserves for biorefining. Appl. Biochem. Biotechnol. (in press).

52.   Mabee, W.E., Gregg, D.J., and Saddler, J.N. (2005). Assessing the emerging biorefinery sector in Canada. Appl. Biochem. Biotechnol. 121: 765-778.

53.   Mabee, W.E., Gregg, D.J. and Saddler, J.N. (2004). Ethanol from lignocellulosics: Views to implementation. Vancouver, BC, IEA Bioenergy Task 39: 90 pp.

54.   MacLean, H.L. and Lave, L.B. (2003). Life cycle assessment of automobile/fuel options. Environ. Sci. Technol. 37(23): 5445-5452.

55.   McCloy, B.W. (2003). Estimated Production, Consumption and Surplus Mill Residues in British Columbia – A 2003 Update. Prepared for Natural Resources Canada. BW McCloy & Associates Inc., Vancouver, BC.

56.   Novozymes. (2005). Novozymes and NREL reduce enzyme cost. Press Release, 14 April 2005.

57.   NRCan. (2006). Renewable Energy Deployment Initiative. Ottawa, ON: Natural Resources Canada, Renewable and Electrical Branch. http://www2.nrcan.gc.ca/es/erb/erb/english/View.asp?x=455. Last accessed Jan. 02/06.

58.   NRCan. (2005a). Canadian Natural Gas: Review of 2004 & Outlook to 2020. Ottawa, ON: Natural Resources Canada, Petroleum Resources Branch.
http://www2.nrcan.gc.ca/es/erb/prb/english/View.asp?x=447. Last accessed Dec. 21/05.

59.   NRCan. (2005b). Renewable Power Production Incentive. Ottawa, ON: Natural Resources Canada, Electricity Resources Branch. http://www2.nrcan.gc.ca/es/erb/erb/english/View.asp?x=681. Last accessed Dec. 28/06.

60.   NRCan. (2003). The State of Canada's Forests 2002-2003, Natural Resources Canada, Ottawa, ON.

61.   OBP. (2003). Multiyear Plan – 2003 to 2008. Office of Energy Efficiency and Renewable Energy/Office of the Biomass Program. Washington, D.C.: U.S. Department of Energy.

62.   Panshin, A.J. and de Zeeuw, C. (1980). Textbook of Wood Technology, 4th ed., McGraw-Hill, Toronto, ON, pp. 213.

63.   Prins, M.J. and Ptasinski, K.J. (2005). Energy and exergy analyses of the oxidation and gasification of carbon. Energy 30(7): 982-1002.

64.   Quirin, M., Gärtner, S.O., Pehnt, M. and Reinhardt, G.A. (2004). CO2 Mitigation through biofuels in the transport sector. Status and Perspectives - Main Report. Heidelberg, Germany, Institute for Energy and Environmental Research Heidelberg: 66 pp.

65.   Rosenberg, A., Kaul, H.P., Senn, T., and Aufhammer, W. (2002). Costs of bioethanol production from winter cereals: the effect of growing conditions and crop production intensity levels. Ind. Crops Prod. 15(2): 91-102.

66.   Sassner, P., Galbe, M., and Zacchi, G. (2005). Steam pretreatment of Salix with and without SO2 impregnation for production of bioethanol. Appl. Biochem. Biotechnol. 121: 1101-1117.

67.   Schulz, M. and Hebecker, D. (2005). Thermodynamic analysis and assessment of bioethanol production. Chemie Ingenieur Technik 77(6): 792-798.

68.   Shanahan, J., Smith, D., Stanton, T. and Horn, B. (1999). Crop residues for livestock feed. Colorado State University Cooperative Extension. Available online at http://www.ext.colostate.edu/pubs/livestk/00551.html.

69.   Sheehan, J.S. and Himmel, M.E. (2001). Outlook for bioethanol production from lignocellulosic feedstocks: Technology hurtles. Agro Food Ind. Hi-Tech 12(5): 54-57.

70.   Skog, K.E. and Rosen, H.N. (1997). United States wood biomass for energy and chemicals: Possible changes in supply, end uses, and environmental impacts. Forest Prod. J. 47(2): 63-69.

71.   Sjöström, E. (1993). Wood Chemistry, Fundamentals and Application, 2nd ed., Academic Press, New York.

72.   Spath, P. and Dayton, D. (2003). Preliminary Screening - Technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. Washington, DC: Department of Energy (NREL), 160 pp

73.   (S&T)2 and Meyers Norris Penny. (2004). Economic, Financial, Social Analysis and Public Policies for Fuel Ethanol. Natural Resources Canada Office of Energy Efficiency, Ottawa, ON.

74.   Statistics Canada. (2004). Environmental Accounts and Statistical Division. Ottawa, ON.

75.   Statistics Canada. (2003a). CANSIM II table 051-0001. Statistics Canada, Ottawa, ON.

76.   Statistics Canada. (2003b). Census of Agriculture. Statistics Canada, Ottawa, ON.

77.   Statistics Canada. (2000). Human Activity and the Environment 2000. Ottawa, ON: Statistics Canada, Catalogue No. 11-509-XPE, pp. 128-130.

78.   Statistics Canada. (1990). CANSIM table 384-0013. Statistics Canada, Ottawa, ON.

79.   Szybist, J.P., Kirby, S.R., Boehman, A.L. (2005). NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy & Fuels 19(4): 1484-1492.

80.   Tijmensen, M.J.A., Faaij, A.P.C., Hamelinck, C.N., and van Hardeveld, M.R.M. (2002). Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. Biomass Bioenergy 23(2): 129-152.

81.   VIEWLS. (2005). Shift gear to biofuels. Utrecht, the Netherlands, SenterNovem: 60 pp.

82.   Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., Manheim, A., Elliot, D., Lasure, L., Jones, S., Gerber, M., Ibsen, K., Lumberg, L. and Kelley, S. (2004). Top Value Added Chemicals from Biomass Volume 1: Results of screening for potential candidates from sugars and synthesis gas. Washington, DC: Department of Energy, 76 pp.

83.   Wingren, A., Galbe, M., and Zacchi, G. (2003). Techno-economic evaluation of producing ethanol from softwood: Comparison of SSF and SHF and identification of bottlenecks. Biotechnol. Prog. 19: 1109-1117.

84.   Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., and Lee, Y.Y. (2005). Coordinated development of leading biomass pretreatment technologies. Bioresource Technol. 96(18): 1959-1966.