The potential of bioconversion to produce fuels and chemicals

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Abstract: Biomass can provide a sustainable and renewable source of transportation fuels and industrial chemicals that may significantly reduce our dependence upon petroleum. The agricultural sector has made significant progress in developing these bio-based fuels and chemicals. Technologies from the agricultural sector may be combined with recent technical improvements that have made wood-based bioconversion more feasible. The bioconversion platform 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.

A biorefinery is an industrial facility able to convert biomass, including lignocellulosic materials such as wood chips, into a range of material, chemical, and energy products, analogous to a petroleum refinery [1]. The petroleum refinery has been in existence for over a century; during that time, the process has become increasingly sophisticated, with the number of products moving from a handful of oils and lubricants to a full suite of materials, chemical products, and fuels. The development of the biorefinery will likely follow a similar route, meaning that as the technology is improved, the opportunities for coproduct generation will expand. The lessons learned in the petroleum refinery will be applied in the biorefinery, however, so the time required for this industry to develop may be significantly shorter. Of equal importance, established markets for various refinery products offer opportunities for bio-based substitutes. Existing pulp and paper mills may be viewed as early examples of the biorefinery, with a strong focus on material products. However, new conversion technologies will allow the continued development of these facilities to enable the production of additional value-added bioproducts, and more efficient recovery of bioenergy.

The biorefinery concept is important because it offers many potential environmental, economic, and security-related benefits to our society. Fuels and chemicals made from lignocellulosic materials are characterized by reduced carbon dioxide emissions when compared to similar products derived from petroleum [2,3], and thus can play a role in meeting Canada's Kyoto Protocol obligations. Expanding existing paper mills, or building new facilities to convert biomass into value-added products, has the potential to create direct and indirect jobs, provide regional economic development, and increase returns to the forest industry [4,5]. Biorefineries offer a sustainable alternative to petroleum reserves which are being consumed at an increasing rate, while the discovery of new reserves is in decline [6]. In some countries, substituting locally-grown biomass for petroleum resources can increase security of supply for chemicals, fuel and energy, by reducing reliance on foreign-owned oil supplies subject to political uncertainty and conflict [7]. In Canada, where domestic oil supplies are relatively plentiful, forest biomass provides a renewable alternative in fuel and chemical production. The sustainable supply of biorefinery products based on woody feedstocks could be a significant portion of Canada's annual demand. The primary barrier to biorefining is generally recognized to be the lack of low-cost processing options (or platforms) capable of converting these polymers into recoverable base chemical components [8]. We will consider two complementary platforms, biochemical and thermochemical, in the sections below.

Bioconversion Platform

In the United States, much of the biomass being considered for the biorefinery includes agricultural crops rich in sugars and starch, and product research has focused on the bioconversion platform [9]. 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, which is a dominant component of cereal crops such as corn and wheat, requires additional processing in the form of an acid- or enzyme-catalyzed hydrolysis step to liberate glucose, but this can be achieved utilizing a single family of enzymes, the amylases, which makes bioconversion relatively simple.

Structural components of plants and trees, including fibres, are composed of lignocellulosic materials [10,11]. In Canada, lignocellulosic biomass will form the majority of available feedstock for the biorefinery. Implementing a bioconversion system utilizing these feedstocks requires some separation of cellulose and hemicellulose from lignin, followed by hydrolysis of five sugars (glucose, galactose, mannose, xylose, arabinose), compared to the single sugar (glucose) associated with starch [12,13]. Because of the increased complexity of the chemical structure, lignocellulosic-based bioconversion is much more difficult and more expensive. Bioconversion offers an economical option to provide high-

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value, low-volume products for niche markets together with lower-value commodity products, such as industrial platform chemicals, fuels, or energy [14,15].

The bioconversion platform combines process elements of pretreatment with enzymatic hydrolysis, as shown in Fig. 1, to release carbohydrates and lignin from the wood. The pretreatment stage must optimize the biomass feedstock by exposing cellulose and hemicellulose for subsequent enzymatic hydrolysis, increasing the surface area of the substrate for enzymatic action to take place. 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 the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI). The pretreatments being considered by the consortia include water-based, acidic, alkaline, and organic solvent pulping systems [16]. 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. 17].

Pretreated biomass is then hydrolyzed, which is typically carried out by enzymes. Enzymatic hydrolysis of lignocellulosics uses cellulases most commonly produced by fungi such as Trichoderma, Penicillium, and Aspergillus [18]. A cocktail of cellulases is required in order to break down the cellulosic microfibril structure into its carbohydrate components in an efficient manner. The enzymatic hydrolysis step may be separated or combined with other stages of the bioconversion process. Separation and fermentation (SHF) offers the platform more flexibility, while simultaneous saccharification and fermentation (SSF) has been found to be highly effective in the production of specific end products, such as bioethanol [17-19].

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 [17].

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. Coordinating 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 [20]. Several pilot or demonstration facilities, each utilizing lignocellulosic-based feedstocks and a bioconversion platform, are currently in existence or are under development, indicating that this process is approaching commercialization. These facilities include the Etek Etanolteknik pilot facility in Sweden, the National Renewable Energy Laboratory pilot facility in the USA, the Abengoa demonstration platform in Spain, and the Iogen demonstration plant in Canada. Most of these facilities have been designed to produce bioethanol, a renewable transportation fuel, as their primary product, but can be configured to examine a variety of co-products.

**THERMOCHEMICAL PLATFORM**

There is a speculation that new advances in gasification technologies could lead to more cost-effective and efficient biofuels or biochemicals through a thermochromical route [21]. This platform uses thermochromical processes to gasify wood, producing synthesis gases (sometimes called producer gases). This platform combines process elements of pretreatment, gasification, cleanup, and a conditioning step to generate a mixture of hydrogen, carbon monoxide, carbon dioxide, and other gases. The products of both platforms may be viewed as intermediate products, which can then be assembled into chemical building blocks and eventually end products [22].

For pyrolysis, pretreatment 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. Biomass gasification itself generally is a two-stage process. In the first stage, the volatile components of biomass are subjected to pyrolysis (combustion in the absence of air) at temperatures ranging from 450° - 600° C. In the lower range of temperatures (450° - 550° C), fast pyrolysis takes place, producing a liquid pyrosylosis oil and very little gas. The oil produced in fast pyrolysis comprises 60-75% of the original fuel mass, and can be used as feedstock for value-added chemical products, or possibly as a biofuel [23]. At higher temperatures, pyrolysis 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 comprises about 10-25% of the original fuel mass. Processing this material requires a second gasification stage. Char conversion occurs at temperatures between 700-1200° C, reacting with oxygen in order to produce carbon monoxide [23,24].

Canada is home to a number of pilot-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 corporate initiatives, such as the plant operated by Enerkom Technologies Inc. [25,26]. In the USA, the Thermochemical Users Facility at the National Renewable Energy Lab is joined by a number of commercial initiatives, including projects led by Georgia Pacific, Boise Cascade, and Mississippi Ethanol LLC [27-30].

**BIOREFINERY OUTPUTS**

**Biofuels**

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. Since 1976, over 80 new ethanol production facilities have been built in the U.S. primarily using corn starch as a feedstock. A Canadian wood-based bioconversion platform has the ability to provide sugars to these existing processes. While starch-based ethanol remains the most cost-effective option, recent advances by the Biomass Refining Consortium for Applied Fundamentals and Innovation indicate that the production costs for lignocellulose-based ethanol can be reduced significantly [see 17].

One of the major proponents of lignocellulose-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 [31]. Other major commercial development in this area is being spearheaded by the Abengoa Corporation, who have partnered with SunOpta Inc. of Ontario on project engineering and development [32].

A previous paper by Mabee et al. [33] estimated the potential levels of Canadian bioethanol production from lignocellulosic sources. Based on a literature review, it was estimated that ethanol yields from lignocelluloses will range between 0.12 and 0.32 L/kg undried feedstock [19,34-36]. It was also estimated that residue generation from the wood processing industry could support the annual production of between 480 million and 1.6 billion litres of ethanol, while forest harvest residues could contribute between 2.3 and 10.4 billion litres of bioethanol every year [33]. Energy plantations on marginal farmland could generate between 1.9 and 11.0 billion litres of bioethanol annually [33]. At the extreme positive range of the scenarios considered, almost all fuel consumption in Canada could be substituted with lignocellulose-based ethanol without impacting agriculture or forestry operations significantly. There is thus great potential for fuel production from biomass using the bioconversion platform.

Until recently, less attention has been paid to biofuels that might be produced through the thermochemical platform. These fuels include hydrogen, methanol, ethanol, and Fischer-Tropsch liquids [37].
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 [21]. This is changing with rising fuel costs and uncertainty about the security of fossil reserves. Large scale development is the key to gaining 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 [37].

Biochemicals

In the past, chemical products were a major part of the forest industry. A number of chemical forest products, based on plant extracts, 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), and rosin (the involatile residues from resin distillation). These products were widely used in wooden shipbuilding & operation, which lent this product category its name of ‘Naval stores.’ About 1.2 million tonnes of rosin worth approximately $400 million (US currency) was produced in 1995, and about 330,000 tonnes of turpentine worth $50 million [38].

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 [37,39]. 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) [40,41].

As previously discussed, biochemical development in the United States is largely based on sugars. 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 [39]. A range of products, including sorbitol, furfural, itaconic acid, glutamic acid, xylitol/arabitol, and glycerol are already prepared commercially. A forest-based biorefinery based on the bioconversion platform could provide inexpensive sugars as feedstocks to these processes.

There are two major projects underway in the US to produce bulk biopolymers for use in textiles and packaging applications. Natureworks LLC produces two polymer products derived from poly-lactide (PLA), including 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 [42]. 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 [43]. E.I. DuPont de Nemours & Co., in partnership with the Diversa Corporation, is developing processes to transform lignocellulosics into 3-hydroxypropionic acid (3-HPA), which can be reduced into 3,3-propanediol [44]. 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.

CONCLUSIONS

The decision on where to invest in infrastructures will very likely be made based on the potential for immediate returns, but it is important to consider the long-term evolution of Canadian pulping facilities towards more diverse biorefineries that are capable of producing fuels and chemicals, as well as energy and a variety of material products. The technological platforms that have been discussed above are complementary, but different. The thermochemical platform is currently most effective at delivering energy, which may reduce operating costs for a mill significantly, but as a product it may not offer high returns to the company in a regulated energy market. The bioconversion platform offers a means to generate sugars from lignocellulosics, which can act as feedstocks for a number of new biochemical products being commercialized today, including ethanol which is in demand as a fuel. This platform can be linked to a number of processes currently being demonstrated for different bioproduct genera-

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