Review of currently available technology for the conversion of woody biomass to value-added products

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ABSTRACT: Much of the pulp and paper industry faces pressure on margins due to decreasing demand in segments such as communication papers. The key question is whether biomass-based high-margin products (over a wide range of oil prices) can be developed as replacements for petroleum products using current pulp and paper infrastructure and skills. Technologies based on sugar, thermochemical, and hybrid and thermocatalytic platforms are summarized in this paper.

Application: Readers can use this material to understand the state of biomass conversion technologies to determine those that need further investigation for their organizations.

Bioenergy Deployment Consortium (BDC) members and the Agenda 2020 Value from Biomass Task Group are developing a roadmap of projects based on marketplace selections to determine preferred technologies [1] to convert woody biomass to value-added products. Similar work focusing on the potential and challenges of drop-in biofuels was recently produced [2]. Technology leaders are addressing three main questions: (1) what focused research and development (R&D) is necessary to enable deployment of these technologies using woody biomass, particularly waste, as feedstock; (2) what focused R&D is required to facilitate integration of these technologies into existing pulp and paper mills; and (3) what other emerging technology pathways are potential candidates for application in the pulp and paper sector and what are the R&D requirements.

SUGAR PLATFORM

The main technologies using a sugar platform for converting woody biomass to value-added products developed over the past two decades are acid hydrolysis, supercritical hydrolysis, and enzymatic hydrolysis.

Acid hydrolysis

Acid hydrolysis has been used for laboratory and pilot operations for decades. The drawbacks include capital cost for special metals, acid recovery, and operating costs. Two companies have been advancing the technology for commercial use.

Blue Fire Renewables used the classic sulfuric acid approach; had access to the pilot facility in Inzumi, Japan; and won U.S. Department of Energy (DOE) awards to build facilities in Lancaster, CA, USA, and Fulton, MI, USA. While the fundamental chemistry was proven, the company was unable to resolve cost issues caused by materials of construction, costly recovery of spent acid, and removal of contaminants. The DOE grants were withdrawn due to missed financing dates and goals. Recently, however, Blue Fire Renewables reannounced the Fulton project.

HCL Cleantech, which developed and patented a process to use and recover hydrochloric acid, received a small DOE grant and constructed a large pilot facility in Danville, VA, USA. The company changed its name to Virdia, conducted successful runs, received an investment from Stora Enso, and announced plans to construct a demonstration plant in Louisiana. It is too early to determine crucial parameters such as capital expenditures (CapEx), operational expenditures (OpEx), yields, and effective use of effluents.

Supercritical hydrolysis

Work on supercritical approaches has been done at several universities (e.g., Auburn) and by Renmatix in King of Prussia, PA, USA. While the technology has been demonstrated, no one has raised funds to complete a demonstration facility. The advantages are the absence of chemical costs; hurdles include isolation of the sugars and removal of contaminants.

Enzymatic hydrolysis

Enzymatic hydrolysis is emerging as the preferred technology when low lignin feedstocks are employed. A large number of companies are involved in developments using enzymatic hydrolysis; many have developed pretreatments to open up the cellulose molecule to allow the enzymes to be more effective. Companies producing enzymes developed more effective and lower cost products. Effective processes were developed for low lignin raw materials. Some companies separated hemicelluloses and processed them separately, but most co-processed them.

The current technology converts 80%-85% of the cellulose and almost all of the hemicellulose to sugars. Yield in gallons of fuel per ton are dependent upon technology and the lignin content of the feedstock. Early approaches attempted the use of lignin as a fuel feedstock to provide process heat. However, solid-fuel boilers are at least one order of magnitude higher in cost than gas boilers. Therefore, most technologies include a gas-fired boiler and include other ways to get value from the resulting products, which include pellets (Dong Energy) and anaerobic digestion (POET-DSM). The progress with low lignin feedstocks was sufficient to permit the construction of a large number of commercial facilities. The same progress has not been achieved with high-lignin feedstocks such as wood.

Much information from this approach can be found at SEKAB in Ornskoldsvik, Sweden. There are very few ongoing efforts to use enzymatic hydrolysis on woody feedstocks. Mascoma has a pilot plant in Rome, NY, USA, and DOE funding for a commercial facility in Kinross, MI, USA. This project has had delays and changes in sponsors. It appears that the tightly bound structures and the high lignin content make enzymatic hydrolysis a less cost-effective alternative for the conversion of woody biomass to value-added products at this time.

Commercial facilities using enzymatic hydrolysis

POET-DSM Advanced Biofuels held a grand opening in September 2014 in Emmetsburg, IA, USA. The plant will produce 20 million gal/year (increasing to 25 million gal/year) of cellulosic ethanol from corn stover. The POET-DSM cellulosic ethanol plant is located adjacent to a 55 million gal/year corn ethanol plant. The stover feedstock is gathered after corn harvest; 75% of the corn crop residue is left on the field, and academic studies have shown that this is sufficient to maintain soil fertility. The smaller size for the cellulosic ethanol plant was selected in part to enable biomass to be gathered from a nominal 45-mile radius around the plant. The process for the corn stover after harvest is pretreatment, enzymatic hydrolysis to sugars, fermentation to ethanol, and distillation. The effluent stream from the cellulosic plant is sent to an anaerobic digester to produce biogas that is used in both plants. The solid stream of lignin is burned in a solid-fuel boiler to produce steam for both plants.

Other commercial facilities in the United States using enzymatic hydrolysis include Abengoa, which will produce 25 million gal/year of cellulosic ethanol and 18 MW of power from wheat straw and agricultural waste in Houghton, KS, USA. The process is similar to that of POET-DSM's process. Residuals are sent to a solid-fuel boiler to produce process heat and power. DuPont started up a 29 million gal/year cellulosic ethanol plant using corn stover in Nevada, IA, USA, in late 2014. The process is similar to that used at Abengoa and POET-DSM.

Quad County Corn Processors is producing 2 million gal/year of cellulosic ethanol using corn-kernel cellulose (a corn-fiber waste product) as the feedstock. The corn-kernel cellulose is a byproduct of their 35 million gal/year corn ethanol plant. The company invented and patented the Cellerate™ process technology and recently granted Syngenta an exclusive license to market the process to other ethanol plants in the United States and Canada. Cellerate technology has the ability to generate 1 billion gal of additional ethanol by adding bolt-on technology to the existing dry-grind ethanol plants without using additional corn. Current hurdles include cost of enzymes, 15%–20% unreacted cellulose, low-value use for the lignin byproduct, a product with a relatively low selling-price, and uncertain continued federal and market support for the product.

Use of sugars

Once cost-effective sugars have been produced, a determination must be made as to their use. Choices are to sell as sugar, ferment to ethanol, or ferment to higher carbon molecules (i.e., chemical intermediaries). It appears that different pathways will emerge for different markets. Although the most popular pathway is toward ethanol, technologies are being developed to produce sugars and chemical intermediates. These developments merit close monitoring. The hurdles are higher cost processes that are more sensitive to contaminants; lower yields; and underdeveloped markets. The preferred technologies will be the ones that give the greatest profit per dollar of feedstock.

Sell as sugar

Without market preferences and incentives, selling the sugar appears promising. Converting sugars to ethanol uses more than 2.2 lb of sugar per lb of ethanol. On a per-ton basis, sugar at half the price of ethanol becomes interesting. A selling price of US$2/gal for ethanol is about US$500/ton or US$0.25/lb; at half the price, sugar is US$0.125/lb. If the cost to isolate or purify sugar is lower than the cost of fermentation, it becomes even more interesting. Before the Old Town Fuel and Fiber facility closed, plans were to construct an ethanol facility in which about 10% of the sugars were to be sold to develop this market for sugars produced with few contaminants; then, the production could be switched from ethanol to sugar [3]. Dong Energy has developed a process to isolate the C_5 sugars and sell them as molasses and convert the other sugars to ethanol.

Ferment to ethanol

Most of the commercial facilities using enzymatic hydrolysis mentioned earlier have selected fermentation to ethanol. The technology is well developed and can be purchased in an engineer-procure-construct (EPC) method with cost and performance guarantees. The major issue is the product's rather low selling price of under US$2/gal. In several countries, there is a government incentive or a promised incentive for selecting this approach; as long as marketplace or government incentives are in place, this will be a popular pathway.

Ferment to higher carbon molecules

Chemical intermediates being considered include iso-butanol, *n*-butanol, succinic acid, and levulinic acid. While the yield is slightly lower, the selling price of butanol is typically three times that of ethanol. It has been cheaper to buy small corn-ethanol facilities and convert them to demonstration scale or commercial scale facilities. Several of those facilities mentioned have business goals to obtain sugars from biomass rather than corn. Most have run pilot trials with those feedstocks.

Facilities worldwide making biochemical intermediates

Bio-succinic acid is being produced by Amyris in France from corn sugars. Amyris is also making 2 million gal/year of farnesene in Brazil. Myriant is making 30 million lb of succinic acid in Lake Providence, LA, USA, from sorghum feedstock. Iso-butanol is being commercially produced from corn sugars by GEVO, which has converted one-third of the capacity of a corn-ethanol plant in Minnesota to make iso-butanol and will convert the remainder later. Green Biologics will conduct a demonstration scale conversion of corn into *n*-butanol in a plant in Iowa, followed quickly by conversion of a corn-ethanol plant in Little Falls, MN, USA, to a commercial scale plant producing *n*-butanol. BioAmber is making 17,000 tons/year of succinic acid in France and has announced a 30,000 tons/year plant in Sarnia, ON, Canada, using corn feedstock.

Solazyme currently has three renewable oil and bioproducts facilities in operation, including a large-scale commercial demonstration foods facility in Peoria, IL, USA; a 20,000 metric tons/year facility in Clinton, IA, USA; and a 100,000 metric tons/year facility in Brazil. In addition, Segetis has a pilot plant in Minnesota making levulinic acid and has converted this product into a plasticizer. The company has a grant to construct a facility with 21.1 million lb/year capacity in Hoyt Lake, MN, USA. Virent received an additional investment from Coca-Cola Company to expand its pilot plant to a demonstration-scale facility to produce para-xylene from purchased sugars. Plant-based para-xylene is expected to pave the way for 100% bio-PET bottles.

THERMOCHEMICAL PLATFORM

The main thermochemical technologies developed in the last two decades are rapid pyrolysis and gasification. As in the case of sugars, the key question is what products will be derived from pyrolysis oil or syngas.

Rapid pyrolysis

Rapid pyrolysis of biomass has been used in laboratories for decades. The biomass is vaporized in the absence of oxygen in seconds and the vapors are condensed to produce a liquid that has numerous molecules, including water. The equipment required has a modest cost, so the CapEx is low at around US$2/gal. Also, the yield is high at 130-140 gal/ton. Pyrolysis oil (sometimes called bio-oil) is acidic and slightly unstable over time. It can be burned as heavy oil, but those commercial applications are limited. A major commercial use occurred when Red Arrow used Ensyn pyrolysis technology to produce pyrolysis oil, then extracted food flavoring (liquid smoke) from it in Rhinelander, WI, USA. Some spent oil was burned to produce process oil and the remaining became a waste stream until a nearby paper mill learned to co-fire it in a conventional boiler [4]. UOP and Ensyn formed a joint venture to refine the rapid pyrolysis oil into transportation fuels. Target dates and products appear to be behind published schedules.

Ensyn also developed a power module. Pyrolysis oil made from woody biomass is burned in a boiler and power is made from a steam turbine. Extraction steam is sold to a local user and power is sold to the grid. These facilities are much smaller than a utility plant and can be successful in situations where a utility will pay a premium for green power and the steam user wants to improve its carbon footprint. One facility is under construction in Dalton, MA, USA. The power meets green requirements for the New England "Yankee network," and Crane & Company will use the steam for process heat.

KiOR used yellow pine as its feedstock, modified the rapid pyrolysis vaporization process by adding a catalyst, and produced modified pyrolysis oil thought to be suitable as a feedstock for a petrochemical refinery. The company announced an 11 million gal/year plant in Columbus, MS, USA, and added processes to convert the modified pyrolysis oil into a drop-in fuel. The capital required was high, with a CapEx of about US$18/gal. The targeted refinery set quality specifications; KiOR set capacity levels. The BDC Critical Success Factor Model (CSF) gave the facility a low rank [5]. The plant started up late and failed to meet quality and yields; it is currently idle.

Cool Planet developed a process that separated the vapors, condensing some into a high-octane gasoline and the remainder into a bio-char that has been demonstrated to promote plant growth. The company has announced a facility in Alexandria, LA, USA, with a capacity of about 10 million gal and a cost of about US$56 million. This gives a facility CapEx of about US$6 per/gal. Some over-the-fence ingredients are not included in the CapEx because they are included in the tolling fee. The facility economics will depend on the sale of the high-octane gasoline additive and the bio-char and stated pricing levels. Cool Planet plans to establish a multitude of these facilities because they are small and can be located in areas where the desired feedstock is available. The CSF model [5] gave the facility a high rank with the assumption that scale-up is under control and the market prices and demand are as stated.

No other major demonstrations or commercial uses of fast pyrolysis have emerged in the United States, and a preferred rapid pyrolysis technology has not emerged. Even if Cool Planet is successful, it will take years to determine whether this technology is preferable to others.

Gasification

The typical gasification process is to dry and size the feedstock, convert the feedstock to a gas, cool and clean the feedstock while recovering heat, and convert the syngas to one or more liquids. Sometimes the initial liquid is further converted to a second liquid.

Gasification has been used in the laboratory for decades. The first major use was with coal feedstock when the German military needed fuel late in World War II. The syngas was cleaned and passed through a Fischer-Tropsch unit to produce gasoline, diesel, and wax. Near the end of the war, volume reached 4 million gal/day. The second major use also used coal as a feedstock. When South Africa was deprived of oil due to embargoes, the South African Synthetic Oil Limited (SASOL) was established in the late 1950s. SASOL built several plants, one of which has a capacity of 7 million gal/year and continues to produce synthetic oil. The low price of petroleum oil has prevented replication of this technology.

There have been numerous successful uses of gasification in the United States, but they were mainly to dispose of products that could not be burned in conventional boilers (e.g., high-silica rice hulls). There was an early demonstration of gasification for the production of transportation fuels by Range Fuels, Soperton, GA, USA. The feedstock was southern softwood and the product was methanol to be converted to ethanol. This facility failed to meet revised targets then failed to meet quantities; however, it produced methanol before it was idled. Some investors stated that the technology was not appropriate for transportation fuels. This facility with a high CapEx ranked lower on the CSF model [5] than other gasification projects, indicating it was a poorly designed facility rather than an improper technology.

The DOE funded gasification projects at Flambeau River Paper and New Page Corporation. Both developed class-20 engineering estimates and converted their targeted feedstock into Fischer-Tropsch diesel and wax in separate 1,000-h continuous hour runs at the ThermoChem Recovery International (TRI) demonstration facility in Durham, NC, USA. Both of these projects failed to receive sufficient funds after the recession of 2008–2010. Successful approaches to major challenges of injecting solid material into a low pressure bed without back leaks and syngas cleaning modules were developed.

The TRI technology was further developed to gasify sorted municipal solid waste (SMSW) and was adopted by Fulcrum for a US$266 million project in Story County, NV, USA. Full details like the value of the recent grant and the power production have not been announced, so any evaluation is premature. This 11 million gal/year facility will produce diesel and aviation fuel and perhaps power. Fulcrum has obtained offtake contracts from Cathy Pacific and expects contracts from the U.S. Navy. The firm has been awarded a US$105 million U.S. Department of Agriculture (USDA) loan guarantee. A federal consortium (including USDA, DOE, and the Navy) has certified the process and awarded Fulcrum a grant. The value of the grant was not specified in the US$212 million October 2014 announcement (if prorated on volume, it will be in the US$20 million range). The CapEx is rather large but the grant and perhaps power production and free feedstock need to be factored into an economic evaluation.

A hybrid technology including gasification has been commercialized. James Gaddy at the University of Arkansas was able to construct a small pilot plant long before the U.S. Energy Independence and Security Act (EISA) of 2007. This facility gasified a variety of biomass feedstocks, performed necessary cleaning, and anaerobically fermented the syngas to ethanol. INEOS purchased the technology and the pilot facility and constructed a facility in Vero Beach, FL, USA, to convert woody biomass and citrus waste to 8 million gal/year of cellulosic ethanol and 6 MW of power. Recently, the plant was retrofitted to add SMSW to the citrus waste and upgrade syngas cleaning. The original CapEx was less than US$16/gal when some capital was allocated to power. The value of the retrofit has not yet been announced.

Meanwhile, Proton Power (a small company in Lenoir, TN, USA) developed a high-temperature process from experience gained in another successful commercialization. Proton Power built a successful 2,000 gal/year facility in Rockwood, TN, USA, to directly convert switchgrass into a drop-in diesel and bio-char. The drop-in fuel has been successfully used in a small conventional diesel-powered generation facility. Other forms of biomass have been trialed. This facility has filed for a permit to build a 4.3 million gal/year facility adjacent to the pilot plant. The US$35 million commercial facility will be modular, so all scale-up has been demonstrated. The gas-to-liquid (GTL) technology is confidential; it is not Fischer-Tropsch. Even at this relatively small size, the CapEx is stated at about US$8/gal. Proton Power has orders for additional units once the first one becomes operational.

No preferred gasification technology has emerged. Hurdles include high capital cost and limited conversion technologies. More details are needed about recent developments. Until then, the low CapEx projects appear to be the more interesting ones.

HYBRID AND THERMOCATALYTIC PLATFORMS

Hybrid technology

The combination of gasification and fermentation is interesting because the higher CapEx of gasification processes is partly offset by lower CapEx of a biological process. INOES has the commercial technology in the United States. In addition, Coskata had an impressive 1.5 million gal/year demonstration facility operating in Madison, PA, USA, gasifying woody biomass and fermenting to ethanol, but it was unable to finance a commercial plant in the difficult financial times during 2008–2010. Coskata closed the demonstration facility and changed its business model to focus on converting low-cost natural gas to fuels. Borregaard has developed a unique separation process (BALI) for economical production of commercial-grade lignin. To enhance the economics, the byproduct cellulose and hemicellulose are fermented to ethanol.

Thermocatalytic technology

The Gas Technology Institute developed IH² technology, an innovative catalytic conversion of woody biomass into gasoline, jet, and diesel fuel (other hydrocarbons can also be made). The products have low acidity, are low in oxygen content, and have less than 1% water. The heating value is 18,000 Btu/lb pound compared with 6,560 Btu/lb with fast pyrolysis oil. Yields are 86-92 gal/ton compared with about 80 gal/ton using enzymatic hydrolysis and gasification approaches [6]. While GTI's DOE-funded project logged over 3,000 h, no one has stepped forward to build a demonstration facility.

Ignite Energy Resource developed a catalytic hydrothermal upgrading approach that converts wet lignite into a bio-crude that can be coblended with fossil crude to produce drop-in fuels. In a pilot plant in Somersby, Australia, Ignite proved that the process could be slightly modified to produce bio-crude from biomass. Licella was formed to capitalize on the woody biomass opportunities. The bio-crude from wood is superior to bio-crude from lignite because it contains all of the chemicals that are in the feedstock, enabling separation and sale of valuable chemicals in the liquid state as value-added products. Ignite won a competitively bid award from the Australian government and will build a 2 million gal/year plant that will have dual capability (lignite and woody biomass). Engineering estimates done with various potential partners show those facilities with single feedstock can have a CapEx of under US$7/gal.

There are no preferred technologies in the hybrid and thermocatalytic platforms. The sample size is too small to state major hurdles.

SUMMARY

There are a number of interesting approaches using woody biomass as feedstock in the production of value-added products. Cool Planet's US$56 million facility in Louisiana will use unique pyrolysis techniques to produce 5 million gal/year of high-octane gasoline and a bio-char which enhances plant growth. Ignite's Licella facility has competitively won a grant to build a commercial scale module with a capacity of 2 million gal/year in Australia. The process will involve a catalytic hydrothermal upgrading approach to liquefy wet wood into bio-crude that can be coblended with fossil crude for petroleum refinery feedstock to produce drop-in fuels. This high-temperature and high-pressure facility will have dual feedstock capability (lignite and woody biomass). Facilities with one feedstock can have CapEx of under US$7 per/gal.

Proton Power has a pilot/demonstration facility to transform available switchgrass directly into a blendable bio-diesel. The unique thermal process avoids Fischer-Tropsch gas-to-liquid conversion. Funding of US$35 million has been obtained to build a 5 million gal/year facility adjacent to the pilot/demonstration plant. Borregaard developed the BALI process to economically produce commercial-grade lignin and cellulosic ethanol. A demonstration plant was built to prove that this lignin would satisfy growing customer demands. As a byproduct of their current operation, Borregaard produces 5.3 million gal/year of cellulosic ethanol. Estimates for cellulosic ethanol from a possible first-of-a-kind BALI plant in the United States are 27 million gal/year [7]. **TJ**

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It is important to help the pulp and paper industry evaluate and consider appropriate research and projects. This paper is more comprehensive and more analytical than previous works.

Because biomass conversion is an emerging industry, there is a lack of reliable technical, financial, and operational information. To verify material, a draft was sent to each company mentioned. We received many excellent comments and incorporated the feedback into our paper. The result is considerable verified information on technologies currently available for deployment.

Mills can focus on the independent variables of feedstocks and markets and select the technology which is most appropriate for an economical conversion. In the current environment, waste feedstocks might be of particular interest. The next steps involve seeking details on technologies and facilities of interest, as well as comparing these opportunities with other technologies such as nanocellulose.

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2014 *TAPPI JOURNAL* Best Research Paper Award

Congratulations to researchers Shisei Goto, Hiromichi Tsuji, Isao Onodera, Keigo Watanabe, and Katsumasa Ono of Nippon Paper Industries in Japan for their paper "Cavitation-jet deinking: A new technology for deinking of recovered paper." The paper appeared on p. 9 of the September issue and was determined the best research paper of 2014 by the *TJ* Editorial Board. It provides new insight into paper recycling technology in terms of reducing dirt speckles and stickies in deinked pulp with minimal fiber damage and describes the apparatus employed.