

The Lignol Approach to Biorefining of Woody Biomass to Produce Ethanol and Chemicals

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Abstract

Processes that produce only ethanol from lignocellulosics display poor economics. This is generally overcome by constructing large facilities having satisfactory economies of scale, thus making financing onerous and hindering the development of suitable technologies. Lignol Innovations has developed a biorefining technology that employs an ethanol-based organosolv step to separate lignin, hemicellulose components, and extractives from the cellulosic fraction of woody biomass. The resultant cellulosic fraction is highly susceptible to enzymatic hydrolysis, generating very high yields of glucose (>90% in 12–24 h) with typical enzyme loadings of 10–20 FPU (filter paper units)/g. This glucose is readily converted to ethanol, or possibly other sugar platform chemicals, either by sequential or simultaneous saccharification and fermentation. The liquor from the organosolv step is processed by well-established unit operations to recover lignin, furfural, xylose, acetic acid, and a lipophylic extractives fraction. The process ethanol is recovered and recycled back to the process. The resulting recycled process water is of a very high quality, low BOD₅, and suitable for overall system process closure. Significant benefits can be attained in greenhouse gas (GHG) emission reductions, as per the Kyoto Protocol. Revenues from the multiple products, particularly the lignin, ethanol and xylose fractions, ensure excellent economics for the process even in plants as small as 100 mtpd (metric tonnes per day) dry woody biomass input—a scale suitable for processing wood residues produced by a single large sawmill.

Index Entries: Lignol; biorefinery; wood; ethanol.

Introduction

The branded name of the technology is the *Lignol Biorefinery Technology*. This technology is an integrated combination of two major generic process elements. The first is an ethanol-based organosolv stage that includes multiple co-product recovery (1), while the second is an

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enzymatic saccharification and fermentation stage that converts cellulose into ethanol, or potentially any other sugar platform chemical.

The technology converts most, if not all, woody biomass residues, from hardwood and softwood sawmill residues to wood chips, and agricultural residues including straw and bagasse. The products of the biorefinery process, in most cases, replace equivalent or identical products currently produced from crude oil, coal, or natural gas, offering significant opportunities for GHG emissions reductions.

Process Description

Woody biomass dominantly consists of three polymeric materials: cellulose, hemicellulose, and lignin, with minor amounts of other lower-molecular-weight materials, such as waxes, resins, fatty acids, and terpenes. Almost always, the three polymers mentioned above represent at least 85% by weight of the dry raw material, but clearly the precise composition is raw material dependent. Factors that influence chemical composition are principally species, geographic, and seasonal-specific. Although cellulose is chemically identical in all species, differing only in its degree of polymerization (DP), the chemical composition and structure of hemicellulose and lignin differs significantly between and sometimes within the three major forms of woody biomass.

When woody biomass is “cooked” under selected temperature and time conditions in a water and ethanol liquor (the so-called organosolv stage), numerous chemical hydrolysis reactions occur, splitting the biomass into its various chemical components (Fig. 1). The preferred conditions depend on the nature of the feedstock being processed, but will generally be in the following ranges: a cooking temperature of 180°–195°C; a cooking time of from 30 to 90 min; a ethanol concentration of from 35 to 70% (w/w); and a liquor to solids ratio of from 4:1 to 10:1 (w/w). The pH of the liquor might range from pH 3.8 to pH 2.0

The largest component, cellulose, a homopolymer of D-glucose, is partially hydrolyzed into smaller fragments that still remain insoluble in the liquor. The second largest component, hemicellulose, a heteropolymer containing hexose sugars (glucose, mannose, galactose), pentose sugars (xylose, arabinose), and acetyl groups is hydrolyzed mostly into soluble components, such as oligosaccharides, monosaccharides, and acetic acid. Acetic acid lowers the liquor pH, stimulating acid-catalyzed hydrolysis of the other components. Some of the pentose sugars are subsequently dehydrated under the operating conditions to form furfural. The quantity of xylose recovered, compared with the amount converted to furfural, is strictly a function of the cooking conditions. A lower liquor pH, a higher cook temperature, and longer cook time will generally reduce the amount of xylose that can be recovered.



Fig. 1. Operating conditions.

The third major polymer component, lignin, is hydrolyzed under the conditions employed in the process mostly into lower-molecular-weight fragments that dissolve in the aqueous ethanol liquor. Minor components of woody biomass, such as the extractives, are also dissolved in the liquor under the operating conditions of temperature and time employed.

These dissolved components turn the "cooking" liquor into a black liquor, which is further processed to:

- precipitate and recover the lignin (by diluting the black liquor with an aqueous process stream and then filtering, washing, and drying the precipitated lignin)
- recover and recycle the ethanol (using flashing of the hot black liquor and condensation of the vapors and then distilling the filtrate and washings from the lignin precipitation)
- recover the acetic acid, furfural, xylose, and extractives (from the distillation column and from the stillage following distillation)
- convert the oligosaccharides into sugars that can be fermented to produce more ethanol (using mild acid hydrolysis).

The insoluble fraction recovered after the organosolv cook consists mostly of cellulose, together with some minor amounts of unhydrolyzed hemicellulose and lignin. This fraction is subjected to enzymatic hydrolysis and fermentation to produce ethanol. The actual yields of the various products is mostly a function of the composition and type of feedstock being processed, but generally the lignin recovered will represent approximately 75–80% of the Klason lignin present in the feedstock. The solids fraction will generally account for all the cellulose of the original feedstock, plus

some hemicellulose and some residual lignin, with the amount of these latter components dependent on the severity of the cook.

The process is most effective on hardwoods and annual fibers, but softwoods can also be processed. For softwoods, more intense cooking conditions are employed, such as a lower liquor pH, a higher cook temperature, and a longer cooking time. Even so, the degree of delignification is usually less with softwoods than with other feedstocks, but the saccharification of the cellulose-rich brownstock is still quite rapid.

This means the original woody biomass is refined, or fractionated, to produce a series of valuable chemicals and fuels, leaving negligible waste and/or low-value material streams. The chemicals required for this process—ethanol and water—are recovered within the process.

Some make-up ethanol is required, owing to minor losses within the process, but this is supplied as a small fraction of the ethanol produced subsequently in the process. Normally, the ethanol recovery is between 98.0% and 99.5% depending on various factors, such as the liquor to solids ratio, in the cooking cycle.

Conceptually, biorefining is equivalent to crude oil refining that is practiced in the oil industry—a barrel of relatively low-value crude oil enters the refining process and is converted almost completely to a series of higher-value fuels and petrochemicals.

Continuous countercurrent operation of the process will lead to numerous advantages over the current batch pilot plant process, as well as potential improvements in the character and performance of the organosolv lignin, because of the lower opportunity for condensation reactions occurring during the cooking stage.

This “improved” organosolv lignin will be examined, formulated and tested in several products to obtain maximum benefit from its anticipated improved performance.

This work involves:

- Simple blending of Lignol organosolv lignin, in both liquid and dry PF resin forms.
- Incorporating organosolv lignin into PF resins during their production.
- Chemically modifying the organosolv lignin to maximize lignin substitution of current panelboard resins (PF resins). The target markets for these products will be oriented strand board (OSB), plywood and particleboard manufacturing.

Until now, the Lignol process has only been operated in a three-stage batch mode and the products are characteristic of this type of operation in that operational and product consistency is difficult to achieve.

Simulation studies indicate a potential for marked improvement of the process economics and its products by converting to a continuous countercurrent mode. This will occur because of higher efficiency, improved process controls and modeling, and more desirable conditions for removal of

the dissolved products from the operating stages of the process. These operating stages require multicomponent optimization in order to minimize undesirable side reactions that reduce the value of the products and lower the economics of the process, such as the unintended conversion of xylose to furfural.

Product Recovery

Area of Application

The technology will be applied in the following areas:

- Forest industry, solid wood—the technology enhances the sustainability of operations as part of the solution to waste wood disposal, and potentially for increased utilization of fiber in woodlands operations.
- Forest products, industrial chemicals—Production of intermediates, specialty, and commodity chemicals. This includes production of biomass-derived substitute for resins used in panelboard and plywood production, reducing formaldehyde emissions.
- Agriculture—The commercialization thrust is focused on wood waste; however, the technology may be developed to process agricultural residues as well. Residues under evaluation include corn stover, corn fiber, flax, sugarcane bagasse, high fiber cane, and guayule. The technology, applied to agricultural feedstocks (4), has the potential to enhance agricultural operations, providing an application as opposed to disposal solution for residues, driving the integration of new sustainable and profitable enterprises in partnership with the agricultural sector.
- Transportation fuel—The production of ethanol and its incorporation into the refining and formulation of various blends of fuel. The technology promises a source of ethanol for the production of reformulated gasoline, a source that may be differentiated in terms of resource efficiency from the commodity production of ethanol from potential food and feed products such as grain and corn.

The Next Steps

The reason that a commercial lignocellulosics-based biorefinery does not exist today is because of the poor economics when ethanol is the sole revenue stream. In the past, cellulase enzymes were expensive and the saccharification rate was very slow for non-pretreated woody biomass. Other processes designed to convert woody biomass into motor fuel ethanol under development tend to depend on steam explosion, or other relatively nonspecific mechanical pretreatment methods, to expose the cellulose for enzymatic hydrolysis. These pretreatment methods, unless supplemented with significant additional processing, mostly eliminate the possibility of

recovering valuable co-products that will add to the revenues of the plant. Therefore, the economics of such plants depend solely on the revenues from the ethanol product, requiring larger plants with greater financial risk and capital investment to justify commercialization.

In the case of the Lignol process, multiple revenue-producing products are recovered (4), so that the total revenues of the plant are significantly greater than the value of the ethanol product alone. In fact, in a Lignol Biorefinery, revenues from ethanol represent only 25–35% of the total revenues of the facility, depending on the raw material. It is the pretreatment using the organosolv stage that provides this enhanced revenue opportunity.

Another reason for enzymatic saccharification now being economically possible is that the US DOE (Department of Energy), in the last 4 yr, has spent approx US\$30 million on helping two major enzyme producers (Genencor International and Novozymes) reduce the cost of producing cellulase enzymes. These companies report that they have reduced the cost of their cellulase enzymes by 10-fold, anticipating a cost reduction corresponding to 20-fold within 2 yr.

These factors alone would not create the commercial feasibility for the Lignol technology if the brownstock (the solid cellulosic fraction from the organosolv pretreatment) from this process were not highly amenable to enzymatic saccharification. The University of British Columbia, Faculty of Forestry (UBC), reported that Lignol brownstock was a highly amenable substrate for enzymatic saccharification and significantly surpassed steam-exploded residues in this regard (5).

Commercial production of ethanol from lignocellulosic materials was practiced for many years in Germany and the Soviet Union in the middle of the 20th century, using variants of the Scholler acid hydrolysis process, which employed hydrolysis with a strong mineral acid, usually sulfuric acid, rather than enzymes. The technology was very inefficient, barely achieving 60% of theoretical yield of ethanol, and highly polluting, since the spent mineral acid required disposal and was very energy intensive to produce. No reasonable opportunity for recovery of a commercially attractive lignin, or other co-product, was possible with this technology beyond its use as an inefficient fuel. In comparison, the UBC Forestry work achieved greater than 90% and sometimes close to 95% of theoretical production of ethanol using the Lignol brownstock substrate. The details of this saccharification and fermentation study are provided elsewhere (7).

The technology development stage of the Lignol process incorporates all of late-stage technical work for commercialization. Key steps are to:

- **Optimize process conditions**— explore different operating parameters for the organosolv cooking process to optimize product yields, product performance, and operating costs. The parameters to be explored include final cooking temperature, residence time for feed-

stock at cooking temperatures, liquor-to-wood ratio, liquor pH, liquor ethanol concentration, and feedstock preparation.

- **Upgrade to continuous production**—operation of the pilot plant to produce the basic process products (cellulose, xylose, lignin, furfural, acetic acid, extractives) using the same realistic feedstock that is most likely to be used in the commercial biorefinery.
- **Optimize product performance**—in particular lignin-based chemicals. Modify process conditions to maximize product performance, product quality and value.
- **Optimize ethanol production**—the enzymatic conversion of Lignol's organosolv cellulose substrate and hemicellulose streams to sugars, then their subsequent fermentation to ethanol, has been performed successfully at the laboratory scale. However, there is still substantial work to be performed in order to optimize the manufacturing cost and the yield. The approach will be to minimize the lignin content of the cellulosic fraction and to explore the opportunity for enzyme recycle in the saccharification stage, while minimizing the inhibition of the cellulase enzymes caused by binding to residual lignin.

Lignol considers the initial markets for its technology and products, over the next 10 yr, as being primarily in North America. Since many potential strategic partners and customers for our end-products operate in both Canada and the US, Lignol believes in focusing there. In the future, there are substantial opportunities in Europe, Asia, and South America to be exploited.

Market Sizes Assumptions (North America)

Ethanol (Fuel Additives Only)

Currently the US market is estimated at US\$7.5 billion. Furthermore, the additional ethanol demand just from MTBE replacement in the state of California only is estimated at US\$1.4 billion. If Canada were to mandate 10% ethanol content in gasoline, that market is estimated at US\$1.65 billion.

The production of ethanol from biomass is greenhouse gas neutral and would assist British Columbia and Canada in achieving current and future greenhouse gas reduction targets (under the Kyoto Protocol) while eliminating the burning of woody forestry residues in beehive burners.

In 1998, Environment Canada concluded there are substantial benefits in providing cleaner burning fuels and reducing smog in Canada.

In the US, the *Clean Air Act* and the Reformulated Gasoline Program mandate the use of oxygenates in 40 metropolitan areas to mitigate carbon monoxide emissions during certain periods of the year. Ethanol is one of the leading oxygenates used, especially now that certain states have banned, or are considering a ban, on the use of MTBE. Both state and

federal governments in the US promote the use of fuel ethanol through a variety of tax incentives. This has stimulated the demand for ethanol.

In 2002, US fuel ethanol production set a new record of 2.13 billion US gallons ($8.05 \times 10^6 \text{ m}^3$) and industry insiders believe production could exceed 3 billion US gallons ($1.13 \times 10^7 \text{ m}^3$) in late 2003 (6). Currently, no less than 34 existing ethanol plants are undergoing expansion, increasing production capacity to 2.7 billion US gallons ($1.02 \times 10^7 \text{ m}^3$) annually. There is presently a Senate Energy Bill before Congressional Committees targeting annual ethanol production of 5 billion US gallons ($1.89 \times 10^7 \text{ m}^3$) in the US by 2012.

Lignin

Organosolv lignin is not comparable to so-called "lignins" currently produced by the pulp and paper industry and others. Its superior properties mean it is commercially useful in a very wide range of applications (2). Unlike lignosulfonates and thioglignins recovered from sulfite and kraft processes (inaccurately but commonly also called lignin), respectively, organosolv lignins contain no sulfur (3). This, together with the narrow molecular weight profile and water repellent properties of organosolv lignins, creates a much higher value lignin product with a much broader range of applications. Lignol's ongoing research has developed opportunities for diverse applications including application-specific adhesives, concrete plasticizers, friction materials for high performance brake products, grease, and asphalt antioxidants and coatings.

All the Lignol biorefinery products with the exception of organosolv lignin are well-known commodities with well-defined specifications as to quality in each category of use. However, organosolv lignin was sold successfully by Alcell in the past (3500 tonnes in total) and received approval for inclusion in the US Toxic Substances Control Act (TSCA) registry. A Lignol biorefinery will produce almost 7000 tonnes of natural, sulfur-free lignin annually for many of the same high-value applications explored and exploited by Alcell.

Xylose

Xylose is a five-carbon sugar widely present in fruit and root vegetables. It is readily converted into a specialty polyol (xylitol) that has about 60% of the sweetness of sucrose and is suitable for diabetics to consume without insulin. Xylitol sells for high value for value added consumer products such as sugarless chewing gums, mints, mouth wash and candy. As planned, a Lignol biorefinery will produce approx 1320 tonnes of xylose annually.

In about 1997, a major xylose supplier analyzed xylose samples prepared from the Alcell process liquors supplied by Repap and would have entered into a purchasing agreement had the commercial mill been constructed. Lignol plans to provide test sample quantities of xylose to prospective customers when the pilot now operating in Vancouver, is upgraded to continuous operations.

Acetic Acid

Lignol estimates there is a US\$1.3 billion market for acetic acid annually in North America. Acetic acid is one of the highest volume chemical commodities sold throughout the world, and is sold commercially in several grades, depending on its purity. It is the basis for manufacturing acetic anhydride for the production of cellulose acetate fibers and membranes. It is also used in the production of vinyl acetate, a raw material used to manufacture latex paint and paper coatings. Acetic acid sells for approximately US\$0.80–1.40 per kg for use in many applications, depending on quality and US/Canada dollar exchange rates. A Lignol biorefinery is expected to produce 650 tonnes of acetic acid annually.

Furfural

Furfural can be used to produce polytetramethylene ether glycol (PTMEG) for the production of Lycra® and Spandex. It is also used to produce lubricants, coatings, adhesives, plastics, and foundry resins for cores and molds to cast metal components as well as conversion to levulinic acid.

US consumption of furfural in 2000 amounted to over 35,000 tonnes. In 2000, 28% of furfural consumption was for the production of furfural alcohol, of which most was used in the production of furan resins. There is no longer a US producer, following the recent shut-down of the Belle Glade, FL, plant formerly owned by Quaker Oats, which used bagasse, a sugar cane by-product, to make furfural. Other former Quaker Oats production facilities used oat hulls to produce furfural.

Overall, US consumption of furfural is expected to grow at a low but constant average annual rate of 2.0% over the next 5 years. Furfural sells for up to approx US\$1.60 per kg. As designed, a typical Lignol biorefinery will produce approximately 650 tonnes of furfural annually, an amount that is not expected to impact the existing market.

Market Forces and Barriers

Ethanol

The dominant ethanol production method in use today in the US and Canada is based on the use of starch-based grain feed stocks (primarily corn). Grain ethanol production costs are currently in the range of US\$0.30–0.45 per liter. In both petroleum and corn processing, about 65–70% of the total production costs are attributable to feedstocks, so in this respect, the use of waste wood is a significant advantage. Approximately 80% of the fuel-grade ethanol produced in North America is from corn. The current price for fuel grade ethanol in California is approx US\$1.50 per gallon (US\$0.40 per liter).

There are a number of companies that are currently exploring the use of lignocellulosic feed stocks from biomass for conversion to ethanol.

These companies include Iogen, BCI, Arkenol, and BRI. Although these companies have made significant advances recently, there is yet to be a full commercialization of biomass to ethanol technology.

Lignol's competitive advantages derive from our biorefining concept that converts the entire feedstock into marketable products. Lignol believes its biorefining technology produces bioethanol at the lowest cost compared with competing technologies.

GHG Discussion: Emissions Impact

Woody biomass residues from the lumber and agricultural industries continue to be incinerated either in beehive burners or, in the case of straw, open field burning. This incineration creates particulates, smoke, and other emissions that are known to impact human health. For this reason, these practices have been banned, or severely curtailed, in many jurisdictions. Furthermore, these practices produce greenhouse gas (GHG) emissions, including carbon dioxide (CO₂), without any practical benefit to man.

In December 2002, Canada ratified the Kyoto Protocol as a signatory nation, in which its CO₂-normalized emissions were to be reduced to 1990 levels. This presents a significant driver for sustainable technology development and implementation in Canada that could well serve as a model for US innovations in the future. By introduction of the Lignol technology, this practice of incineration and its resultant emissions can be economically eliminated.

Furthermore, the products produced by the Lignol biorefining process almost entirely replace products currently produced from fossil carbon sources, such as oil, natural gas, and coal. Ethanol produced by this process replaces ethanol produced from natural gas condensates and substitutes for existing gasoline oxygenators made from oil and natural gas that have higher environmental impacts in motor fuels.

Conclusion

Lignol's challenge is a familiar one—convincing customers to change to a new and superior product. The current interest both in industry and among consumers on environmental improvement is a strong motivator in Lignol's favor. Organosolv lignin, in particular, provides superior environmental characteristics compared with the products it is intended to displace.

In summary:

- At C\$25 million annual revenue per plant, Lignol's market share in each market addressed will be small, even when several plants are in operation, thus causing minimal market disruption.
- Lignol is building a series of relationships with strategic partners in the forest industry and the energy industry that will open markets for its products such as ethanol and lignin.

- Many oil refiners blend ethanol into their gasoline now or plan to in the near future.
- Forest product companies are potential suppliers of feedstock in the form of wood residues.
- Many also are producers of composite wood products and are interested in organosolv lignin as a substitute for PF resins used in manufacturing products such as oriented strandboard (OSB), as well as coatings, friction materials, antioxidants, and concrete plasticizers.
- The Kyoto Protocol will provide significant momentum and benefit to the commercialization of the Lignol model.

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