High Yielding Biorefining using Organosolv Processing

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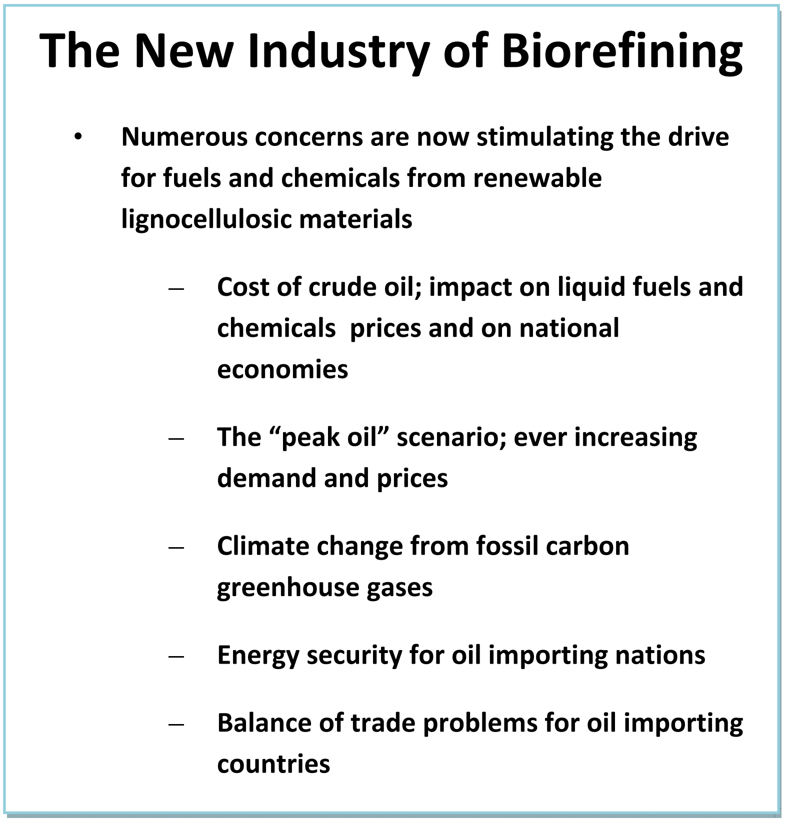
Introduction

Various economic, environmental and political forces have combined to create an unprecedented change in the world economic order in less than a single decade. Rapidly expanding economies in the world's most populous nations have created a large consumer-oriented middle class resulting in an increased demand for energy, higher quality foods and material resources. These factors together with mounting evidence that sources of easily and cheaply obtainable oil are declining, has led to rapidly escalating crude oil prices, which have doubled during the past year. Within the developed countries other pressures, such as supply concerns, national security, balance of trade issues and environmental problems including global warming, have led to recent legislation and the commercial development of alternative forms of energy, especially renewable energy. Various forms of renewable energy, including wind, solar, tidal and biomass-derived liquid transportation fuels, are now undergoing rapid commercialization. The most immediate problem facing the US general population is the rapidly escalating price of liquid transportation fuels, home heating fuels and secondarily the price of oil and natural gas-derived chemicals and materials. These are having a highly inflationary effect on prices in general and food prices in particular.



The New Industry of Biorefining

- **Numerous concerns are now stimulating the drive for fuels and chemicals from renewable lignocellulosic materials**
  - **Cost of crude oil; impact on liquid fuels and chemicals prices and on national economies**
  - **The "peak oil" scenario; ever increasing demand and prices**
  - **Climate change from fossil carbon greenhouse gases**
  - **Energy security for oil importing nations**
  - **Balance of trade problems for oil importing countries**

The New Industry of Biorefining

As a consequence of these factors there has been a dramatic expansion of corn-based ethanol facilities in the US. By the end of this year, approximately 170 such facilities should be in production with an annual production capacity greater than 9 billion gallons of ethanol. Ultimately, according to the 2007 US Energy Independence and Security Act a total of 15 billion gallons of corn-based ethanol will be required by 2022. However, that same act mandates that there should be an additional 21 billion gallons of "Advanced Biofuels" of which

16 billion gallons should be from lignocellulosic sources. This calls for an enormous construction effort, which will introduce a totally new national industry of biorefining of cellulosic materials such as wood, agricultural residues, deliberately grown energy crops, and the like.

Biorefinery Concepts

Lignocellulosic biomass, the structural components of plants such as tree trunks and cereal straw, is now the primary focus of the developing biorefining industry because it represents the lowest cost and largest potential volume of any plant material on the planet. Vast quantities of woody agricultural residues, such as straw and corn stover, are presently either left in the field or incinerated for no value. Such materials are composed primarily of three biochemical polymers. The most abundant one is cellulose, a homopolymer of the sugar D-glucose, linked by a β, 1-4 linkage. A lesser polymer is hemicellulos*e*, a complex polymer consisting of various hexose and pentose sugars, together with acetyl groups and uronic acids. The third polymeric component is lignin that is made up of variously modified phenylpropane moieties linked by numerous types of linkages including carbon-carbon bonds and aryl-alkyl ether linkages. In addition to these primary components of woody biomass, there are minor components including various lipophylic compounds generally grouped under the heading of “extractives” that include resin acids, terpenes, fatty acids and phytosterols. Many minor components of woody biomass have been the source of valuable chemicals that have found uses in medicine (e.g. salicylic acid, β-sitostanol, etc.), in food (e.g. arabinogalactan), and in materials (e.g. turpentine).

Biorefineries capable of processing these relatively recalcitrant lignocellulosic feedstocks can use many different technologies. A conceptually relatively simple one is the gasification of biomass to create syngas, which can then be converted into a somewhat limited range of organic chemicals by chemical or biological means. Pyrolysis is another thermochemical process that creates a range of gaseous, liquid and solid products. Like gasification, pyrolysis has the advantage of being relatively insensitive to the type of feedstock, but both of these thermochemical processes significantly degrade the complex chemical components in lignocellulosic biomass, many of which have potentially high commercial value in their original form.

Other biorefinery processes utilize strong or dilute acids, steam or alkali to open up the compact cellular structures in woody biomass, thus exposing the fiber wall polysaccharides, cellulose and hemicellulose, to enzymatic attack. Most of these processes target the production of hexose and pentose sugars derived from the hydrolysis of cellulose and hemicellulose for conversion into fermentation products such as ethanol, butanol, lactic acid, etc. The remaining impure biomass components, such as lignin, rosin and resin extractives, etc. are then mostly used as low value solid fuel to power the process.

Organosolv Biorefineries

Organosolv technology, as used in the ethanol-based Lignol Modified Organosolv Biorefinery Process, allows for the fractionation of lignocellulosic biomass into a series of valuable chemical products, which have a combined commercial value that greatly exceeds the value of a variety of fermentation products made from just the carbohydrate fractions of woody biomass alone. The advantages of this value-retention strategy are numerous. With greater revenues being obtained from each unit of feedstock, such plants require smaller amounts of resource to be profitable, thus avoiding the need for large harvesting areas and opening up many more suitable locations for biorefineries. This has the added advantage that profitable plants can be smaller, thus requiring a lower total capital investment, which is a considerable advantage for an early stage technology. Furthermore, the revenues of such a plant are less dependent on the potentially-variable market values of any one single product, such as ethanol. The process treats woody biomass, - softwoods, hardwoods, agricultural residues, deliberately grown energy crops, etc. – with an aqueous ethanol liquor at elevated temperatures. The precise conditions are dictated by the nature of the feedstock, the desired product streams and process energy considerations.

The lignin and hemicellulose in the biomass are partially hydrolyzed and dissolve into the liquor, while the hydrophobic “extractives” also dissolve in the hot organosolv liquor. Some additional chemistry occurs in the process, such as the conversion of some pentose sugars from the hemicellulose into furfural, but generally, most of the fine chemical structures originally in the biomass are preserved. Following the modified organosolv stage, a solid fraction consisting mostly of cellulose with minor amounts of residual lignin and hemicellulose is ready to be converted by enzymatic hydrolysis into a sugars stream useful for various fermentation processes. Because most of the lignin has been removed, this cellulose-rich fiber mass is more readily hydrolyzed by enzymes than are equivalent streams from other biorefinery processes. This “pulp” stream can also be processed further into a number of commercially-useful chemicals and materials, such as cellulose derivatives and powders. The liquor from the organosolv stage is processed to recover separate streams of high-purity lignin (HP-L™ lignin) for use in resins and a large number of other applications, as well as furfural, acetic acid from the hemicellulose, wood “extractives”, pentose and hexose sugars and oligosaccharide products. The ethanol used in the process is recovered by distillation and recycled back to the process. Energy for the process, - steam and electricity only – can be provided from co-generation facilities burning bark and forestry residuals. No fossil carbon fuel is required for the process. The net water consumption of the process is negligible.

The unit processes that make up the Lignol Biorefinery are combinations of well-known processes that currently exist in either the chemicals, biochemicals or pulp and paper industry. Some, but very little new process equipment is required, assuring a high degree of confidence in its operability and performance. A large 70 tonne of feedstock per day demonstration plant utilizing a substantial portion of this technology has been operated for many years in the past. The multi-product, value-retention approach to biorefining has numerous technical and economic advantages, which will be discussed.

The Lignol Biorefinery technology, which is able to process softwood, hardwood and annual fibers, consists of two principle steps (Figure 1). First is a modified solvent extraction stage that treats biomass with an aqueous alcohol liquor at elevated temperatures and pressures for a specified time. This treatment converts much of the large lignin polymers in the woody biomass into smaller molecular weight fragments, which dissolve in the hot alcohol-based liquor. These fragments still retain most of the chemical structure and properties of the original lignin, but unlike lignin extracted from wood in the kraft and sulfite pulping industry, they do not have sulfur introduced into their chemical structure. Thus the lignin extracted from biomass by the Lignol technology still retains many valuable properties above and beyond its aromatic content and finds high value commercial markets.

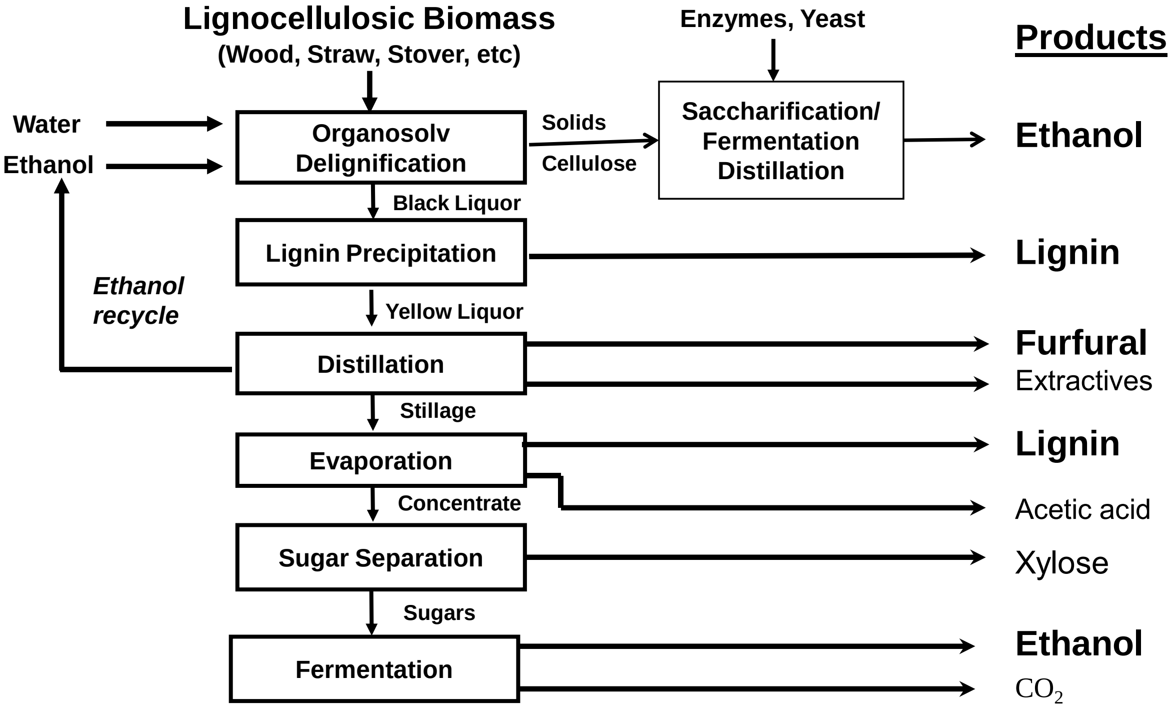


Figure 1. The Lignol Biorefinery Process

A number of other important reactions occur during this first extraction stage of the Lignol Biorefinery process. Acetic acid, furfural and various hexose and pentose sugars arise from reactions involving hemicellulose. Additionally, most of the lipophylic components of the biomass, generally called “extractives”, appear in the hot liquor. The products of this first stage, therefore, are a cellulose-rich fiber and an aqueous alcohol liquor containing the extracted materials. This liquor is then treated in a series of unit processes to recover the ethanol; the industrial chemical furfural; a valuable extractives fraction; additional lignin fractions and the hemicellulose hexose sugars, which can be fermented to produce ethanol. Acetic acid, a widely used industrial chemical, can also be recovered from the liquor.

The second stage of the Lignol Biorefinery process is the conversion of the cellulose in the fibers to glucose, a process called saccharification, and then the fermentation of this glucose to produce ethanol. Due to the relative purity of the cellulosic fiber fraction that results from this process, Lignol uses a cellulase enzyme complex to perform the saccharification. This results in very high yields and conversion rates that cannot be achieved with acid catalyzed saccharification. The yeast that is employed in the fermentation has been carefully selected by Lignol to allow rapid ethanol production from both the cellulose-derived glucose as well as certain hexose sugars derived from the hemicellulose.

As can be seen, the Lignol Biorefinery creates high value from the biomass feedstock by producing multiple co-products together with high yields of fermentable sugars that are readily converted to fuel ethanol, or other “sugar platform” chemicals. This is achieved to a great extent by preserving the structure and then recovering most of the chemicals that nature created in the biomass. Many other biorefinery processes currently under development, utilize only the sugars obtained from the cellulose and sometimes the hemicellulose, and then burn the remainder to create steam and power for the process. This provides something less than solid fuel value to the plant. There are many other materials, less amenable to biorefining, such as bark, that can provide fuel to a biorefinery.

The Lignol Biorefinery process has numerous advantages that result mostly from its production of multiple co-products. The revenue from these additional products creates an economic advantage that can be exploited to allow the technology to be viable in relatively small plants. This opens up the prospect of locating these biorefineries in large sawmills to use the wood residues created at these operations, or placing them within pulp mills where excess wood chips could be made available. Certainly, this technology holds the promise of creating significant value from fuels and chemicals derived from lignocellulosic biomass and should be a leading technology in the new rapidly developing biorefining industry.

Pure Lignin – A Product of Organosolv Biorefineries

As one of the three major polymers always present in woody biomass, lignin represents a considerable proportion of the structural components of plants. It can account for approximately 10-12% of the aerial portion of some short annual plants and up to 30% or more for some coniferous trees. As such it is claimed to be the second most abundant organic chemical on earth [and is therefore a major renewable chemical that should not be overlooked, either in volume or value. Significant commercial markets, totaling over one million tons per year, already exist for lignins that have been recovered from chemical pulp mills . The value of lignin in these markets is generally an order of magnitude higher than its fuel value. With the anticipated future construction of biorefineries processing lignocellulosic feedstocks, the amount of lignin potentially available for marketing for its chemical value, rather than its fuel value, is likely to be enormous. Furthermore, lignin from some types of biorefineries will most likely have better performance characteristics and be of greater commercial value for its chemical properties than lignins from existing chemical pulping operations. The availability of these “new” lignins with enhanced physical and chemical properties will no doubt stimulate major new markets for this renewable material. However, it is likely that these materials will find their initial markets in the same sectors as the current lignin products. A review of the manufacturing, properties and present markets for lignins from pulping operations is therefore instructive in assessing the potential economic value of lignin that might be recovered from biorefineries processing lignocellulosic materials.

A simple examination of the chemical structure of native lignin [shows some interesting similarities to the structure of phenol-formaldehyde resins. Lignin consists of a three-dimensional amorphous matrix of cross-linked phenylpropanoid units. These residues, depending on their botanical source, may have, to a greater or lesser extent, substitution of methoxy groups on the ortho positions to the hydroxyl group on the aromatic ring. Lignin from annual plants, with a high proportion of ρ-hydroxy phenylpropane residues, will have a significantly lesser degree of o-substitution, while lignins from hardwoods, with a high content of syringyl moeties, will have a high proportion of o-substituents on the aromatic ring. Softwood lignin with a high content of guaiacyl groups (more than 90%) and some p-hydroxy phenylpropane moieties will have a greater degree of methoxy substitution.

Both native lignin and phenol-formaldehyde resins are polyphenolic materials consisting of phenolic rings linked together by short aliphatic chains. However, the form of these linkages in lignin are much more diverse and different from the linkages in PF resins. In lignin many of the cross-linking groups are aryl-alkyl ethers, but there are numerous carbon-carbon links also. Furthermore, lignin has a significant number of functional groups, such as aliphatic hydroxyls, on the propane residues, a feature that is not shared with phenolic resins. Nevertheless, the structural similarities are close enough to suggest a strong compatibility between these two materials and even opportunities for chemical interaction between them, with or without added cross-linking agents. Lignosulphonates and thiolignins have been marketed for incorporation into phenolic resins for some time, but they do not appear to have met with significant acceptance by the resin industry.

Some of the problems experienced by current lignins in this market may be overcome with biorefinery lignins, but not by all forms of biorefinery lignins. Organosolv processing of woody biomass can readily yield a non-derivitized lignin having high purity, significant chemical reactivity, low polydispersity and low molecular weight. Organosolv lignins from hardwood produced in tonnage quantities by the Alcell process in Miramichi, Canada, in the 1990's has been readily substituted into phenolic resins and used successfully on a commercial basis. Commercial applications in which it was used included in phenolic resins used in OSB manufacture and the production of friction materials. Numerous other applications where organosolv lignin was being substituted in part or in whole for phenolic resins were also under development at that time, such as in saturating resins for laminates production, stiffening agents for container boards and in rubber processing additives.

The manner of substituting lignin for phenol-formaldehyde resins can vary from a) a simple blending of dry powder lignin with dry powder phenolic resin, to b) the use of organosolv lignin as a primary phenolic component during the manufacture of the resin. In both cases the lignin represents the substitution of a renewable material for non-renewable chemicals produced from fossil carbon.

The advantages to the users and suppliers of phenolic resins of partial or complete substitution of biorefinery lignin are numerous. They include the potential of lower cost raw material and the opportunity to receive valuable carbon credits since phenolic resins are produced from phenol, now almost totally produce from crude oil, and formaldehyde, which is a product of natural gas. In addition, recent studies have shown that the incorporation of organosolv lignin into PF resins that are used in the manufacture of OSB will reduce the emissions of formaldehyde from the press during manufacture. This is a major advantage to manufacturers because these emissions of a known carcinogen are being closely monitored and regulated by various governments. A added benefit to OSB manufacturers is that it has been shown that the substitution of up to 35% of PF resin with an equal weight of organosolv lignin will provide substantial improvements to the final board properties, especially in reduced swell of the wet board and a higher modulus of rupture following the boil test.