Chemicals from Biomass with Novel Tunable Solvents

Science Article***:*** http://www.sciencemag.org/cgi/content/short/311/5760/484

We are currently investigating the production of value-added chemicals from biomass using tunable solvents which offer unique process advantages, coupled with specialty separations to obtain a multitude of targeted compounds which can be sold as is or further processed to value-added chemicals. Current methods of producing value-added products from biomass are implemented on a small scale but are simply not economically competitive with oil-based alternatives. Using the unique properties of benign, tunable solvents, we are developing economically viable, sustainable methods for biomass conversion. Although the focus here is on woody biomass, the technique developed may readily be extended to other forms of biomass, such as a variety of agricultural wastes.

This project demonstrates the potential of renewable resources benefiting both the environment and the economy. It will develop a new method for harvesting high value-added chemicals from renewable resources which has the potential to revitalize the United States forest products industry, vastly increasing its international competitiveness while decreasing our dependence on foreign petrochemicals. Partnering with pulp and paper industries will insure that our processes are economic and compatible with existing facilities.

We are investigating methods of recovering value added chemicals from biomass with tunable solvents, including **G**as-e**X**panded **L**iquid (**GXL** - CO_2-expanded methanol), supercritical fluids (**SCF** - CO_2, methanol, and dimethyl ether), and nearcritical water (**NCW**). Tunable solvents offer significant opportunities for improving both operating economics and environmental sustainability of chemical production, plus the ability to tailor the chemistry of the process to facilitate desired reactions. These solvents are especially good at penetrating solid matrices, providing a host of unique extraction opportunities. Following extraction, specialized separations will isolate targeted chemical compounds, mixtures and product streams, taking advantage of the properties of the solvents used and novel methods of compound-specific separations. The targeted value added chemicals are wide ranging from specialty chemicals, pharmaceutical precursors and flavoring agents (Vanillin, Syringol, Syringaldehyde) to large scale commodity chemicals, including candidates from the DOE's "Top Value Added Chemicals from Biomass" (2004). Interaction with industrial partners will facilitate the transfer of these new technologies for the conversion of low-value forest biomass into high-value chemical compounds.

Value Added Chemicals from Black Liquor

Vanillin	**0.30 mg/ml**	**$5/lb**
Syringol	**0.29 mg/ml**	**$15/lb**
Syringaldehyde	**0.58 mg/ml**	**$25/lb**

We have demonstrated the extraction and fractionation of vanillin, syringol, and syringaldehyde from commercially available wood lignin using GX-Methanol. Figure 1 below demonstrates this fractionation based on composition as a function of CO_2 pressure or composition. As the CO_2 composition increases, the specific lignin components precipitate out of solution as shown by the color change in the collected extractant at different processing pressures. At 38 bar of CO_2, 99.95% of the lignin polymer is precipitated out of the gas expanded methanol. The fractionation is based on the relative solubility of the different lignin components in the GXL due to molecular weight and chemical functionality. The future extension of this process will be to isolate additional value added chemicals from black liquor pulping waste as well as other biomass streams. This technique will enable facile integration of our proposed technology with an existing chemical process within a paper mill. The isolation of valuable compounds from waste streams exemplifies the major goal of sustainable processing: integrating economic and environmental goals within the chemical industry.

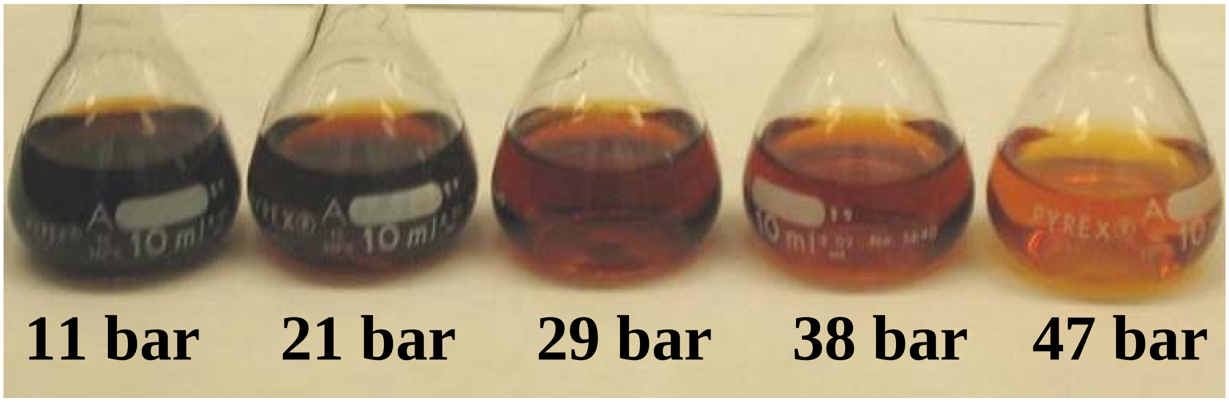


Figure 1. Fractionation of Organosolve Lignin (Sigma-Aldrich) in methanol with increasing CO_2 pressures. At 38 bars of CO_2 99.95% on the lignin mass has been precipitated, demonstrating the selective precipitation of lignin components based on relative solubility.

Industrial application of these methods will involve extracting value added chemicals (value $5-25/lb.) from a pulp and paper mill black liquor side stream (from lignin, value 2-3¢/lb.). Using a small fraction (15-20%) of this stream, to minimize mill disruption, we project a net profit after capital and operating expenses of about $5 million for a single mill. The economic potential is for a 72% return on investment. The application of our specialty solvent systems can be divided into three areas, each of which exhibits specific qualities.

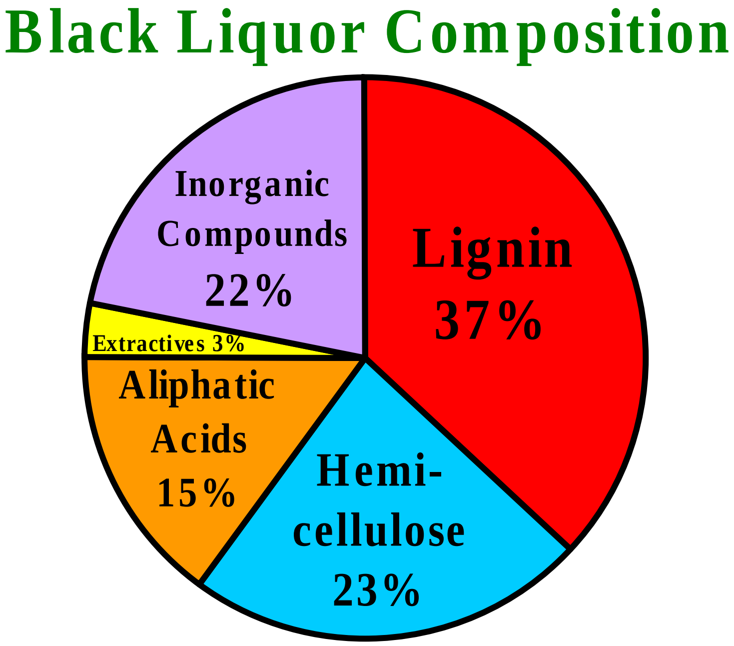
Extraction – The extreme penetrating power of SCF and GXL solvents will increase extraction efficiency. Also, we shall adjust temperature, pressure and resonance time for thermophysical control over extractant distribution and composition. Further we use self-neutralizing acids which aid in the reactive digestion of lignin-cellulosic material and avoid waste salts from neutralization.

Separation – We can perform compound-specific separations using advanced multi-phase processes. The adjustable solvent strength of GXLs and SCFs will enable selective precipitation on the relative solubility of each compound, with facile and benign solvent removal and recovery, as well as natural product isolation.

Chemical Conversion – We plan to use NCW for chemical oxidation and depolymerization as well as conversion of glucose to levulinic acid, a proposed renewable platform chemical. Examples include peroxycarbonic acid, a self-neutralizing reagent from CO_2 with H_2O_2[1], for the oxidative conversion of glucose to glucaric acid, and use SCW for the conversion of waste biomass to clean syngas.

Applications with Industry

The kraft pulping process is the preeminent pulping technology in the U.S., and the capital investment associated with this process requires that any changes in pulping and papermaking retain this key process[2,3]. Despite the well-acknowledged advantages of kraft pulping (i.e., high-strength pulps, insensitivity to wood species; ease of recovering spent pulping chemicals/energy) it operates with several process limitations, including relatively low pulping yields of 40-45%. Although the loss of lignin is a favorable outcome during pulping, the loss of hemicelluloses is unfavorable. Hemicelluloses contribute little to the heating value of black liquor but detrimentally increase the viscosity of black liquor. The isolation and fractionation of lignin and hemicelluloses from black liquor, followed by conversion into targeted value added chemicals through the use of novel technologies will revitalize the U.S. pulp and paper industry. Both black liquor and wood extract streams constitute a substantial source of lignin and hemicellulose, which will be processed by similar methods based on their chemical composition and the targeted chemicals. Since the ultimate use of lignin and hemicellulose is fuel, at a value of 3¢/lb., clearly its conversion to high value-added products is most desirable.



The forest products industry, broadly defined as those manufacturing sectors of the economy that convert wood into consumer products, has a significant contribution of 5% to the U.S. GDP and provides employment in many rural one-industry towns that are critically dependent upon their natural wood resources. However, due to recent pulp and paper market conditions 28 pulp mills have been decommissioned and their capital infrastructure remains a very attractive basis from which biorefining pilot trials and implementation programs could be developed. Furthermore, many of these plants are located in rural areas that have suffered chronic unemployment and yet have ample wood and/or agricultural waste residues. The development of biorefinery technologies utilizing this shuttered capacity would be one of the few technological solutions that would avoid the $0.5 – 1 billion of new investment costs needed to develop a biorefinery capable of processing 1,000 - 2,000 tons of wood per day. These biorefinery plants would employ excess regional wood resources including wood thinnings that need to be removed from this nation’s forests to reduce the threat of catastrophic forest fires.

This research will develop innovative methods to diversify the range of products that can be efficiently and cost-effectively produced from biomass. A vital component of the overall research program will be the development of an educational outreach program that will teach the next generation of scientists, engineers and business leaders about the science/technology and social issues concerning biomass refining. The introduction of these new techniques for production of high value-added chemicals will help restore the competitive edge of the U.S. forest products industry, in both national and international markets.

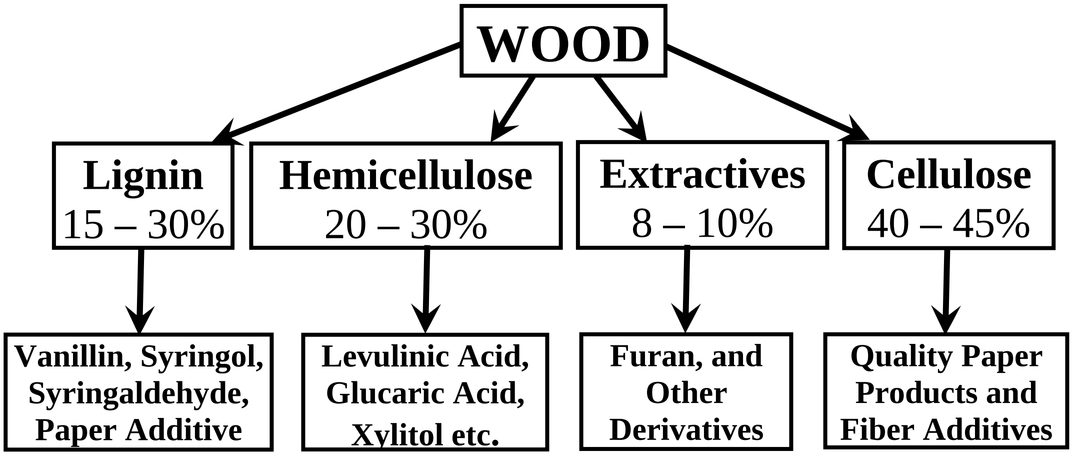
The integration of our research with the forest products industry will create both immediate and long term opportunities by developing methods that work in conjunction with existing working paper mills or as stand-alone processes. Both applications are centered on using novel extraction, separation, and chemical conversion systems to produce high value-added chemicals. A breakdown of each follows:

Paper Mill Application – This method is designed for short term application to work in parallel with existing paper mills with little capital costs and no interruption of mill operation. The goal is to take a slip stream (5 to 20%) from the black liquor waste stream and extract targeted compounds that will either be sold as is or converted to value-added specialty chemicals. We foresee this application providing substantial profit to U.S. paper mills, ensuring their continued operation and expansion.

Stand-Alone Process – This approach is further reaching in span, magnitude, and time frame where the technologies we develop will be applied to forest products biomass by targeting high value-added specialty chemicals and materials for production. The range of products includes specialty chemicals, commodity chemicals, and quality natural fibers. The process is clean, does not use sulfur compounds or inorganic acid catalysts, and is sustainable, consuming all types of wood biomass.

Technical Approach/Research Plan

The following diagram demonstrates the goal of this project to fractionate wood biomass based on chemical composition and structure.



The four proposed extraction streams include:

Lignin extracted with GXLs and fractionated to vanillin, syringol, syringaldehyde, and paper additive.

Hemicellulose extracted with GXLs and processed with NCFs to produce glucose, mannose and xylose for chemical conversion to glucaric acid, levulinic acid, xylitol, etc.

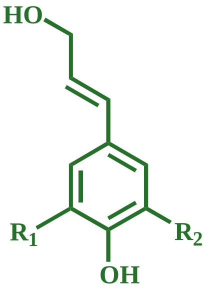
Extractives extracted with GXLs and yielding furan and other derivatives for potential sale or conversion to value-added chemicals, polymer and pharmaceutical precursors.

Cellulose Fibers remain after extraction to be sold as pulped, processed, high quality natural fibers for textiles, additives, or paper products.

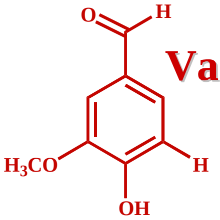
The techniques developed through this work will be versatile with applications either in series with existing forest product industries, such as paper mills, or as a stand alone process for waste forest product biomass. With respect to stand alone processes, an in depth analysis on wood chip extraction will determine a population of targeted chemicals to isolate from the extract, purify and chemically convert to value-added products. This approach will extend to a wide range of product markets beyond specialty and commodity chemicals. Cellulose fibers from the extraction phase will be sold as high quality fibers, for which a market currently exists. The extractives stream holds potential for obtaining additional value added chemicals. Other researchers are developing methods to obtain valuable chemicals from wood extracts and may be implemented in conjunction with this research[4,5]. Unused biomass material can be converted to clean synthesis gas by SCW gasification techniques. Synthesis gas is a valuable commodity for the production of clean hydrocarbon fuels and represents a major source of hydrogen and carbon feedstocks.

Lignin – Lignin is the second most abundant biopolymer found in nature and the biosynthesis of lignin stems from the polymerization of three types of methoxylated phenylpropane molecules, specifically coniferyl, sinapyl, and *p*-coumaryl alcohol. The deligninification on depolymerization process involved with wood digestion yields a variety of phenolic compounds. Three primary structures that we are targeting are vanillin ($5/lb), syringol ($15/lb), and syringaldehyde ($25/lb) which are ideal value-added chemicals present in black liquor and readily obtained from delignification processes.

Lignin: polymerized phenylpropane groups

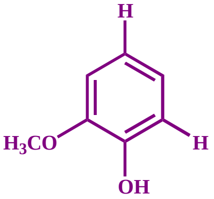


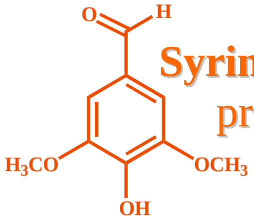
Coniferyl Alcohol; **R_1= OCH_3 R_2= H**
Sinapyl Alcohol; **R_1= R_2= OCH_3**
p-Coumaryl Alcohol; **R_1= R_2= H**



Vanillin: flavoring, chemical & pharmaceutical precursor

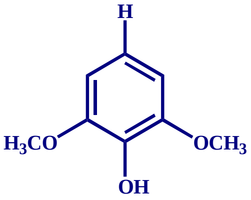
Guaiacol: smoke flavor, pharmaceutical precursor





Syringaldehyde: pharmaceutical precursor, hair & fiber dye

Syringol: smoke flavor, natural meat preservative



Hemicellulose – Wood based hemicelluloses are linear, amorphous polymers of sugars with molecular weights less than that of cellulose, consisting primarily of xylans and glucomannans, 5 and 6 carbon sugars. The most abundant hemicelluloses are xylans, which are present in all terrestrial plants and comprise 15-30% of hardwoods and 5-10% of softwoods. Glucomannans exist mainly in softwoods (15-25%)[3]. Following extraction and fractionation of the hemicelluloses from the wood biomass or black liquor, the xylan fraction can be processed with nearcritical water to produce levulinic acid and its derivatives. These chemicals can then be isolated and/or subjected to further chemical conversion. The glucomannans will also be processed with nearcritical water, resulting in glucose and mannose; the glucose will be oxidized to glucaric acid using peroxycarbonic acid (CO_2 addition at mild pressure to the aqueous solution with hydrogen peroxide). Recent industrial applications of this technology include the Biofine Process for the conversion of cellulosic waste to Methyl THF to be used among other things, as a gasoline additive up to 60% by volume.

The Biofine process was developed by BioMetics, Inc. and funded by the DOE –EERE Industrial Technologies Program and the Forest Products Industry of the Future strategy with goals in line with Agenda 2020 Technology Alliance (http://www.agenda2020.org/). Biofine was awarded the 1999 Small Business Presidential Green Chemistry Award. A pilot plant, built in South Glens Falls New York, has been operating since 1998. A commercial plant is near completion in Caserta, Italy.

The Biofine process uses two-step dilute mineral acid hydrolysis to break down lignocellulose biomass three main chemicals, furfural, levulinic acid, and lignin. The levulinic acid and furfural is concentrated and recovered, the acid catalyst is recycled, lignin is fed to a gasifier to make hydrogen. The furfural and levulinic acid are purified and hydrogenated to make MeTHF.

Tunable Fluids

Alternative solvents for chemical extraction and processing of biomass offer significant opportunities for improvements both in operating economics and in environmental control. Many of these opportunities are being realized by using benign solvents with readily tunable solvent properties, such as supercritical fluids, **G**as-e**X**panded **L**iquids (GXLs) and **N**ear**c**ritical **W**ater (NCW). We shall also use benign, self-neutralizing acids, such as dissociated water, methylcarbonic acid, and peroxycarbonic acid.

Specific advantages of using these solvents include:

- Environmentally benign - low cost, low toxicity, low waste, energy efficient
- Opportunities to use "natural acids" via formation of alkylcarbonic acids (GXLs) or increased hydronium (oxonium)/hydroxide (alkoxide) ion concentration (SCF MeOH, NCW). The formation of these acids is reversible; thus no neutralization/waste disposal is required
- Opportunities to perform mild oxidation without catalysts through production of peroxycarbonic acid from hydrogen peroxide and CO_2
- Facile separations and product purification using the tunable nature of solvents with pressure, and temperature
- Enhanced opportunities in crystallization using gas antisolvent techniques
- Direct extraction and selective fractionation of natural products
- Reductions in solvent usage and fugitive emissions from chemical processing
- Ease of scaling and implementation – many similar processes are now in use

Supercritical carbon dioxide ($scCO_2$) is an effective replacement for organic solvents[6,7]. However, it requires high pressures and exhibits limited solvation of high molecular weight compounds[8]. GXLs, composed of CO_2 and a cheap, benign, expandable organic solvent (such as methanol) overcome these limitations. GXLs operate at much lower pressures, penetrate matrices well, and show improved solvent power and similar control of solvation selectivity[9]. GXLs have also found use as reaction solvents[10] and have been shown to form reversible alkylcarbonic acids *in situ* from CO_2-expanded alcohols and used for catalytic applications[11]. These properties make GXLs a promising new solvent alternative for chemical processing. We are using GXLs for the selective extraction and fractionation of valuable intermediates from biomass.

Nearcritical water, 250-350 ºC, offers exciting possibilities as a benign solvent for the synthesis of organic chemicals. As water is heated to near its critical region, the fluid expands and takes on several useful properties [12,13]. It dissolves both salts and organic chemicals, enabling homogeneous aqueous/organic reactions[13-17]. Further, the separation following the reaction becomes simple; cooling the mixture causes the organic chemicals to come out of solution to be decanted[18,19]. Also, as the temperature is increased, the dissociation constant for water, K_W,[20] goes up by orders of magnitude; the water itself is both a natural base and acid, and can catalyze reactions[20], avoiding subsequent neutralization and salt disposal. We plan to use nearcritical water to generate a self-neutralizing acid for the depolymerization of hemicelluloses and the dehydration of intermediates.

Hydrogen peroxide (H_2O_2) has been used for various applications from bleaching to organic synthesis[21]; however, its application to oxidative synthesis is limited without catalytic activation or conversion to a more reactive peroxy acid. Metallic catalysts and peroxy acids[21] are common ways to activate peroxide, however, problems with catalyst stability, safety, and byproduct formation provide additional processing challenges and expenses. Due to the drawbacks associated with both metallic catalyst and conventional peroxy acid catalyzed epoxidations, we developed a process that can overcome these difficulties by using the simplest possible activated hydrogen peroxide species, peroxycarbonic acid[22]. It is well known that CO_2 reacts with water to form carbonic acid[23]. By analogy, the reaction of CO_2 with hydrogen peroxide should generate peroxycarbonic acid[24]. We propose to generate peroxycarbonic acid using this *in situ* technique and use it as a mild oxidant for conversion of extracted glucose to glucaric acid.

We have goals of applying these novel tunable solvents for the extraction, fractionation, and chemical conversion of forest product biomass to value-added chemicals. Currently, we are using GXLs to extract lignin and hemicelluloses (glucomannan and xylan) from wood and black liquor. The role of CO_2 in the extraction process is to resolve mass transfer limitations, significantly reducing extraction time and increasing efficiency. The use of reversible acids with GX methanol is a key aspect for the digestion of the wood biomass for the extraction process. Current methods use mineral acids for digestion which pose issues with post-process neutralization, waste disposal and product contamination. After extraction, the solvent properties of the GXL extract will then be tuned (via changes in temperature and pressure) enabiling acid neutralization and the selective precipitation of lignin, glucomannan and xylan, purifying these compounds for further processing.

Scalability and Implementation

The long term goal of this research is to develop economic methods of biomass conversion into value-added products that are competitive with current oil-based products. Current methods of producing valuable products from renewable resources have been implemented on a small scale but are limited and simply not economically competitive with oil- and coal-based alternatives. This project uses benign, tunable solvents to facilitate economically viable, sustainable methods for the selective extraction and conversion of wood biomass into multiple streams of targeted platform compounds and value-added chemicals derived from the platform compounds. Solvents such as supercritical fluids, nearcritical fluids, and gas-expanded liquids provide process advantages not only for extraction and separation, but also for benign reaction processes and catalysis.

Benign tunable solvents of the type proposed here are already in wide usage. Currently there are more than 100 processes worldwide using supercritical CO_2[25] including food processing (coffee decaffeination, hops extraction), polymerization, fluoropolymer synthesis by DuPont, hydrogenation by Thomas Swan, coatings initially by Union Carbide (now Dow), and polyurethane processing by Crain Industries. Concomitantly, other tunable solvents are being used in a variety of applications: nearcritical CO_2 for dry cleaning, nearcritical propane for soil remediation, very hot water (and others) for cleaning microelectronic elements, and gas-expanded liquids for particle production, pharmaceutical processing and neutraceutical extraction.

Systems using tunable solvents are readily scalable, and it is quite common to use laboratory data with process design programs (such as ASPEN) to do successful designs for full scale plants. Laboratory measurements are used to understand mechanisms and to determine rates of reactions, rates of mass transfer, and phase equilibria. These data are then incorporated into the design program for scale-up. We can demonstrate the scale-up calculations using our small-scale data to design a system 1-2 orders of magnitude larger. Then in conjunction with our industrial partners, we can then verify scale-up on a larger scale.

Transfer of technology and implementation of the results are vital for this research. We must not only make the forest products industry aware of the results, but also facilitate their adoption. For this reason we partner with industry through selected representatives. Coordinated academic-governmentindustry interaction will ensure that the research tasks will remain relevant to the needs of the forest products industry, growing industrial sector utilizing renewable biomaterials, and society in general.

Environmental and Economic Benefits

For those states that are dependent upon the forest industry as a main contributor to economic health and employment, current forest products industry trends are alarming. For states such as Georgia, Wisconsin, Maine, Alabama, Arkansas, and others; the loss of pulp mills has led to substantial increases in rural unemployment and reductions in future economic growth. Despite the challenging economic conditions of today, tremendous new opportunities are developing with new technologies. The conversion of the plastics industry from hydrocarbon-based technologies to carbohydrate-based would dramatically improve rural employment opportunities, enhance national security, and improve environmental performance, including reductions in CO_2 emissions. Many of these societal benefits were recognized by David Morris who coined the term "carbohydrate economy" 15 years ago[26]. It was envisaged that by shifting society's engine toward renewable, environmentally benign materials, agro/forestry-based manufacturing enterprises would provide several positive ramifications:

- Pollution would be no longer be generated from extracting and processing crude oil into chemicals.
- End-of-life disposal would not be an issue, as the products are completely biodegradable.
- Manufacturers would no longer be saddled with high hazardous waste disposal costs, lengthy permit processes, and compliance costs.
- Biomaterials derived from forest resources will prevent the generation of 100×10^6 tons of CO_2 annually from oil products.

The net result is a process which will upgrade waste hemicellulose and lignin from a waste fuel to a series of high value-added chemicals by environmentally and economically conscious methods. The use of novel, tunable solvents for the extraction, fractionation and chemical conversion of forest products biomass will ensure the economic viability of the U.S. forest products industry for the next millennium. The environmental benefits of using our proposed solvents are paramount; they are truly sustainable as they are both benign and economically advantageous. An additional benefit of obtaining the proposed chemicals from biomass involves oil displacement. Currently, one million pounds of levulinic acid are produced annually, and the potential exists to increase drastically the world market for levulinic acid by providing a sustainable source from renewable resources. Modern industrial techniques utilize petrochemical feedstocks for the production of levulinic acid. Switching to a biomass-based process would represent significant displacement of petroleum-based feedstocks for levulinic acids and other chemicals from biomass.

Applying cutting edge chemistry and engineering to the current methods of biomass conversion will enable the production of competitive bio-based products, drastically increasing the demand and reducing our dependence on oil. Successful implementation of these methods will provide large quantities of chemicals which currently cost \$5 per pound on average, but increased availability and production at less than \$0.50 per pound will generate new applications and greater demand. Our methods are capable of producing large quantities available at competitive prices and providing the United States with an enormous source of revenue from a renewable resource.

An initial economic analysis has been performed for the incorporation of a component of this process into an existing paper mill which produces 1000 tons of pulp per day. The analysis assumes 40% extraction of the hemicelluloses which make up 30% of the wood chip mass[2] followed by a 15% conversion of the extracted hemicelluloses to product. The current market value for levulinic acid is

$5 per pound[27,28]; however for this analysis we assume a market value of $0.50 per pound based on a decrease in price with increased production and comparison with the market value of potential replacements such as acrylic acid. The economic analysis projects a $12.8 million total capital investment with a 72% rate of return and 17 month payoff period from product sales of $14.6 million per year. Thus the proposed process is quite competitive with other acid-catalyzed methods of levulinic acid production.

Major Equipment	**5,838,135**		Production	
Fixed Capital	**11,676,271**		**Wood Chip Feed (tons/day)**	**2222**
Working Capital	**1,167,627**		**Hemicellulose % of Wood**	**30**
Total Capital	12,843,898		**Extraction Efficiency, %**	**40**
			Product Conversion, %	**15**
Operating Costs			**Total Product, #/yr**	**29,197,080**
MeOH Losses (1%)	**1,546,512**		**Product Price ($/lb)**	**0.5**
CO_2, Water Losses (3%)	**355,520**		**Total Income ($/year)**	**14,598,540**
Labor,Overhead (4 shifts/wk.)	**400,000**		Net Income Before Taxes	9,302,187
Energy (2000 BTU/# Product)	**1,709,931**			
Amortizaiton (10 years)	**1,284,390**		**Return On Investment**	**72**
Total Operating Costs	5,296,353		**Payoff Period, Months**	**17**

Long Range Outcomes

The utilization of biomass for the production of biofuels and high-value chemicals is a growing national and international research priority. Significant motivation for this research includes our nation’s dependency on foreign petroleum imports that are frequently acquired from unfriendly and/or unstable geopolitical locations. Indeed, a review the nation’s petroleum requirements/production capacity indicates that since approximately 1960 our demand needs have consistently outstripped production capacity. For example, in 1970 the nation required 63 quadrillion BTU of fossil fuels of which 30% was imported. By 2000 this had grown to 72 quadrillion BTU of which approximately 50% was secured from foreign sources.

It is anticipated that by 2005 the nation will be dependent on fuel imports for 62% by 2020. The nation cannot produce its way out of this high dependence on hydrocarbon imports as national oil production peaked in the late 1960’s and has declined approximately 1%/year. This dependency on fuel imports yields an oil import bill of $60 billion in 1999 and will grow to $110 billion by 2010. Clearly, the development of innovative biomass refining technologies that reduce imported petroleum products would dramatically enhance this nation’s national security, balance of trade, and environmental performance including net reductions in CO_2 emissions. It would also utilize one of this nations most valuable natural renewable resource, agro/ forest products, thereby providing a re-growth of rural employment and economic health.

These benefits were clearly acknowledged in Presidential Executive Order 13134, titled “Developing and Promoting Biobased Products and Bioenergy” and have begun to impact the national economy. For example, Congress recently passed legislation requiring refineries to raise their usage of biobased ethanol in gasoline from 1.8 billion gallons annually (Note: 96% derived from corn) to 5.0 billion gallons annually within a decade. The successful introduction of corn-derived polylactic acid (PLA) into the marketplace (120×10^6 kg annually) by Cargill is another example of the evolution of the carbohydrate economy. These products and others utilize plant carbohydrates for biofuel/biochemical production.

Another important consideration is President Bush's initiative to restore forest health and prevent catastrophic wildfires which was formulated in response to the forest fires suffered by this nation in 2002. This law expedites forest thinning projects on some 20 million acres of federal land and legislates $760 million for forest thinning projects, providing copious additional low-cost wood. Forest Service thinning estimates for the Western US are about of 1.5 billion tons oven-dried trees.

Applying cutting edge chemistry and engineering to the current methods of biomass conversion will enable the production of competitive bio-based products, drastically increasing the demand and reducing our dependence on oil. The use of wood products will also provide forest-rich portions of the US with an enormous source of revenue from a renewable resource. This research embodies innovation through the development of new technologies with educational advancement on many levels to ensure future economic and environmental sustainability.

(1) Nolen, S. A.; Lu, J.; Brown, J. S.; Pollet, P.; Eason, B. C.; Griffith, K. N.; Glaser, R.; Bush, D.; Lamb, D. R.; Liotta, C. L.; Eckert, C. A.; Thiele, G. F.; Bartels, K. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 316.

(2) Johnson, T. G.; Steppleton, C. D. "Southern Pulpwood Production, 2002," U.S. Department of Agriculture, 2002.

(3) Sjostrom, E. *Wood Chemistry, Fundamentals and Applications*, 2nd ed.; Academic Press Inc.: San Diego, 1992.

(4) Kostamo, A.; Holmbom, B.; Kukkonen, J. V. K. *Water Res.* **2004**, *38*, 972.

(5) Umezawa, T. *Chemistry of extractives*; Marcel Dekker, Inc.: New York, N. Y, 2001.

(6) Eckert, C. A.; Chandler, K. *J. Supercrit. Fluids* **1998**, *13*, 187.

(7) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. Supercritical Fluids as Solvents for Chemical and Materials Processing. In *Nature*, 1996; Vol. 383; pp 313.

(8) Musie, G.; Wei, M.; Subramaniam, B.; Busch, D. H. *Coord. Chem. Rev.* **2001**, *219-221*, 789.

(9) Reighard, T. S.; Olesik, S. V. *Crit. Rev. Analytical Chem.* **1996**, *26*, 61.

(10) Blanchard, L. A.; Brennecke, J. F. *Green Chem.* **2001**, *3*, 17.

(11) West, K. N.; Wheeler, C.; McCarney, J. P.; Griffith, K. N.; Bush, D.; Liotta, C. L.; Eckert, C. A. *J. Phys. Chem. A* **2001**, *105*, 3947.

(12) Akerlof, G. C.; Oshry, H. I. *J. Am. Chem. Soc.* **1950**, *72*, 2844.

(13) Kuhlmann, B.; Arnett, E.; Sisken, M. *J. Org. Chem.* **1994**, *59*, 3098.

(14) Bröll, D.; Kaul, C.; Kramer, A.; Krammer, P.; Richter, T.; Jung, M.; Vogel, H.; Zehner, P. *Angew. Chem. Int. Ed.* **1999**, *38*, 2998.

(15) Chandler, K.; Deng, F.; Dillow, A. K.; Liotta, C. L.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1997**, *36*, 5175.

(16) Chandler, K.; Liotta, C. L.; Eckert, C. A.; Schiraldi, D. *AIChE J.* **1998**, *44*, 2080.

(17) Lesutis, H. P. *Chem. Commun.* **1999**, 2063.

(18) Brown, J. S.; Hallett, J. P.; Bush, D. M.; Eckert, C. A. *J. Chem. Eng. Data* **2000**, *45*, 846.

(19) Chandler, K.; Eason, B.; Liotta, C. L.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 3515.

(20) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295.

(21) *Ullmann's Encylcopedia of Industrial Chemistry*; 5th ed.; Elvers, B.; Hawkins, S.; Ravenscroft, M., Eds.; VCH: New York, 1991; Vol. A19, pp 199.

(22) Thiele, G.; Brown, J. S.; Nolen, S. A.; Eason, B. C.; Lu, J.; Eckert, C. A.; Liotta, C. L. Process for the Epoxidation of Olefinic Compounds US, 2000.

(23) *Kirk-Othmer Encyclopedia of Chemical Technology*; 4th ed.; Kroschwitz, J. I.; Howe-Grant, M., Eds.; John Wiley and Sons, 1991; Vol. 5, pp 35.

(24) Khidirov, S.; Aliev, Z. *Izobreteniya* **1993**, *18*, 60.

(25) Beckman, E. J. *J. Supercrit. Fluids* **2004**, *28*, 121.

(26) Morris, D.; Ahmed, I. *The Carbohydrate Economy: Making Chemicals and Industrial Materials from Plant Matter*; Inst for Local Self Reliance, 1992.

(27) *Top Value Added Chemicals From Biomass - Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; Werpy, T.; Petersen, G., Eds.; Department of Energy: Office of Biomass Program, 2004; Vol. 1, pp 69.

(28) Fitzpatrick, S. W. Production of levulinic acid by the hydrolysis of carbohydrate-containing materials.; Biofine Incorporated, U., Ed. USA, 1996; Vol. US 1995-475630; pp 19.