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Top Value-Added Chemicals from Biomass

Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin

[1] JE Holladay   [2] JJ Bozell
[1] JF White   [3] D Johnson

[1] Pacific Northwest National Laboratory
[2] University of Tennessee
[3] National Renewable Energy Laboratory

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Top Value Added Chemicals from Biomass

Volume II: Results of Screening for Potential Candidates from Biorefinery Lignin

Produced by Staff at
Pacific Northwest National Laboratory (PNNL) and
the National Renewable Energy Laboratory (NREL)

J. J. Bozell, J. E. Holladay, D. Johnson, and J. F. White
Principal Investigators

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List of acronyms

AFEX	ammonia fiber explosion
AQ	anthraquinone
Btu	British thermal unit
BTX	benzene, toluene, xylene
CF	clean fractionation
DMAQ	dimethylanthraquinone
DME	dimethyl ether
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DOE	United States Department of Energy
EE	Energy Efficiency and Renewable Energy, an office in the Department of Energy
FDA	United States Food and Drug Administration
FT	Fischer-Tropsch
g	gram
gal	gallon
kg	kilogram
lb	pound
LD50	median lethal dose
LMW	low molecular weight
LP	liquid propane
MIBK	methyl isobutylketone
Mn	number-average molecular weight
MTBE	methyl tert-butyl ether
MTG	methanol-to-gasoline
MTO	methanol-to-olefins
NREL	National Renewable Energy Laboratory
OBP	Office of the Biomass Program, a program in DOE EERE
PAN	polyacrylonitrile
PF	phenol-formaldehyde
pH	potential of hydrogen
PNNL	Pacific Northwest National Laboratory
RVP	Reid Vapor Pressure
TAME	methyl tertiary-amyl ether
Tg	glass transition temperature
WGS	water gas shift
yr	year

Executive Summary

This report evaluates lignin's role as a renewable raw material resource.

Opportunities that arise from utilizing lignin fit into three categories:
- power, fuel and syngas (generally near-term opportunities)
- macromolecules (generally medium-term opportunities)
- aromatics and miscellaneous monomers (long-term opportunities)

Biorefineries will receive and process massive amounts of lignin. For this reason, how lignin can be best used to support the economic health of the biorefinery must be defined. An approach that only considers process heat would be shortsighted. Higher value products present economic opportunities and the potential to significantly increase the amount of liquid transportation fuel available from biomass.

In this analysis a list of potential uses of lignin was compiled and sorted into "product types" which are broad classifications (listed above as power—fuel—syngas; macromolecules; and aromatics).

In the first "product type" (power—fuel—gasification) lignin is used purely as a carbon source and aggressive means are employed to break down its polymeric structure. In the second "product type" (macromolecules) the opposite extreme is considered and advantage of the macromolecular structure imparted by nature is retained in high-molecular weight applications. The third "product type" (aromatics) lies somewhere between the two extremes and employs technologies that would break up lignin's macromolecular structure but maintain the aromatic nature of the building block molecules.

The individual opportunities were evaluated based on their technical difficulty, market, market risk, building block utility, and whether a pure material or a mixture would be produced. Unlike Volume I of this report, "Top Value Added Chemicals from Biomass, Volume I: Results of Screening for Potential Candidate from Sugars and Synthesis Gas" (commonly called the Sugars Top 10 Report), it was difficult to identify the ten best opportunities, however, the potential opportunities fell nicely into near-, medium- and long-term opportunities. Furthermore, the near-, medium- and long-term opportunities roughly align with the three "product types." From this analysis a list of technical barriers was developed which can be used to identify research needs.

Lignin presents many challenges for use in the biorefinery. Chemically it differs from sugars by having a complex aromatic substructure. Unlike cellulose, which has a relatively simple substructure of glucose subunits, lignin has a high degree of variability in its structure which differs according

1

to the biomass source and the recovery process used. In addition to its structural variability lignin is also reactive and to some degree less stable thermally and oxidatively compared with other biomass streams. What this means is that integrating a lignin process stream within the biorefinery will require identifying the best method to cost-effectively separate lignin from biomass.

Moving forward we offer seven points of consideration:

(1) Lignin offers impact. Since lignin constitutes up to 30% of the weight and 40% of the fuel value of biomass it can be used to increase fuel production. It offers higher revenues to biorefineries through production of products rather than power. However, the technology needs to be developed to realize lignin's potential.

(2) There is a balanced R&D portfolio of near- medium- and long-term opportunities, each with their own technical challenges.

(3) Some technology is available for lignin use now. Thermochemical processes can be used with many lignin streams in the near to medium term. Also some of the macromolecular opportunities, identified as medium-term, exist today.

(4) The most effective use of DOE funds will be in broadly applicable technology development. Medium- and long-term opportunities will require transcending some significant barriers.

(5) Development of selective and robust catalytic processes to selectively break and make bonds will be an important area of technology development.

(6) In addition, other technical support is also required and at least as important. This includes lignin conditioning, structure analysis and separations technology.

(7) Perhaps the most important point is this: technoeconomic analysis is required to determine the value proposition of lignin utilization beyond power and should be a driving force to guide research efforts in this day of limited budgets. This will allow us to uncover opportunities in the shortest time.

1 Background

America is fortunate to possess abundant and diverse agricultural and forest resources, unused cropland and favorable climates. Together with a remarkable talent to develop new technologies, we have a tremendous opportunity to use domestic, sustainable resources from plants and plant-derived resources to augment our domestic energy supply.

The Biomass Program, in the Energy Efficiency and Renewable Energy Office of the U.S. Department of Energy (DOE) directly supports the goals of The President's National Energy Policy, the Biomass R&D Act of 2000 and the Farm Security, Rural Investment Act of 2002 and the Energy Policy Act of 2005. To accomplish these goals, the Biomass Program supports the integrated biorefinery, a processing facility that extracts carbohydrates, oils, lignin, and other materials from biomass and converts them into multiple products including fuels and high-value chemicals and materials. Wet and dry corn mills and pulp and paper mills are examples of biorefinery facilities that already produce some combination of food, feed, power and industrial and consumer products.

This report, the second of several envisioned to examine value-added products from all biomass components,[1] identifies possible lignin-derived materials and chemicals that could serve as an economic driver for a biorefinery. In addition, technical areas are identified that would need to be developed to make uses of lignin feasible.

Integrating the production of higher-value chemical/material co-products into the biorefinery's fuel and power output will improve the overall profitability and productivity of all energy-related products. Increased profitability makes it more attractive for new biobased companies to contribute to our domestic fuel and power supply by investing in new biorefineries. Increased productivity and efficiency can also be achieved through operations that lower the overall energy intensity of the biorefinery's unit operations; reduce overall carbon dioxide emissions; maximize the use of all feedstock components, byproducts and waste streams; and use economies of scale, common processing operations, materials, and equipment to drive down production costs.

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[1] Volume I of this series examined candidates from sugars and synthesis gas, see "Top Value Added Chemicals from Biomass, Volume I: Results of Screening for Potential Candidate from Sugars and Synthesis Gas." T. Werpy and G. Peterson, Eds., August 2004. http://www.nrel.gov/docs/fy04osti/35523.pdf

2 Objective

The objective of this report is to evaluate lignin's role as a renewable raw material resource, whether it be generation of power or production of fuels and chemicals. From the evaluation an outcome of this report is the suggestion of research needs for DOE.

Lignocellulosic-based biorefineries are integral to a sound domestic policy for a safe and secure energy future. At the highest level, biorefineries input biomass as carbon sources and can generate fuel, power and products as output (Figure 1).
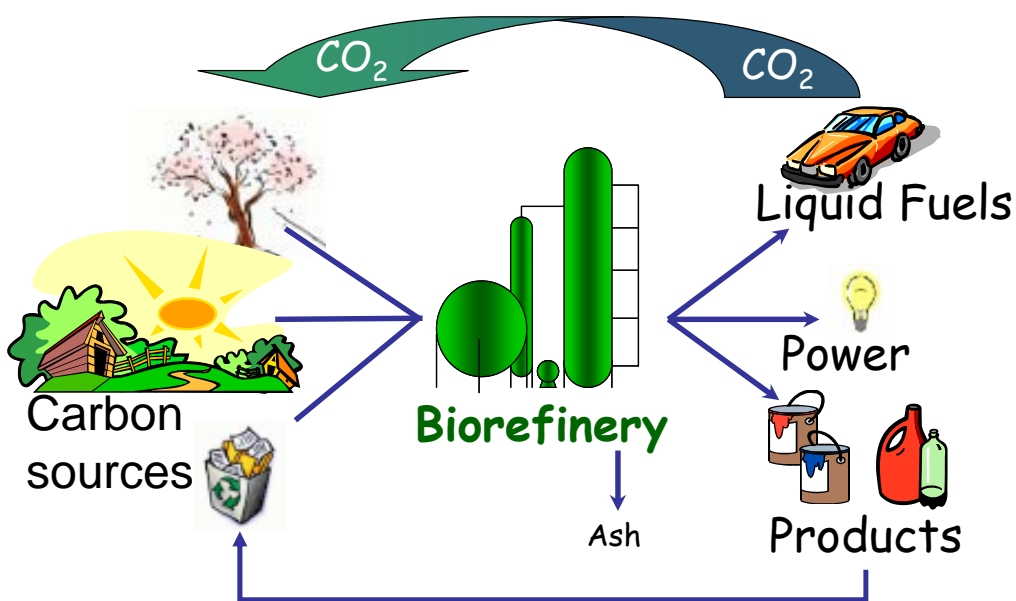
Figure 1 - Biorefinery Concept

In this construct, biomass is separated into its component parts: sugars (as cellulose, hemicellulose or starch), lignin, protein and oils. In various current biorefinery concepts, the sugar or oil fractions are used to produce liquid transport fuel or products while lignin is most often relegated to low-value uses of combustion. In fact, in the currently operating biorefineries lignin is either burned to produce process heat and recover pulping chemicals in paper mills or sold as a natural component of animal feeds in wet or dry corn mills.

Biorefineries will receive and process massive amounts of lignin. For this reason, how lignin can be best used to support the economic health of the biorefinery must be defined. This report identifies applications and uses for lignin starting with process heat and proceeding to chemicals and materials. Because the report considers where DOE research might play a role, products that have exceptionally high value but very low volume, such as in the

pharma sector, fall outside the scope of this report. Additionally, products in the food sector, such as the use of purified lignin as a food additive (neutraceutical), are not considered.

Applications and uses of lignin are categorized into, near-term, medium-term, and long-term opportunities and attempt to identify research areas where DOE support will have the greatest impact.

Where information is available, the report attempts to clarify the current economics of products from lignin and lignin-rich resources using chemical, biochemical or thermochemical processes. The report identifies which product classes are currently more favorable and which might have the most impact on petroleum displacement and the economic viability of biorefineries. However, the key to the report is identification of R&D breakthroughs (near-, medium-, and long-term) needed to make the biorefinery more economically attractive through better use of lignin.

Investigating and understanding the structure, types, sources, and production methods for lignin, as well as its past and current applications, will help identify specific opportunities that meet DOE's overall goals of energy independence and petroleum displacement. A compendia of such information is provided in the appendices of this report.

There appears to be an entrenched myth in industry that "you can make anything you want out of lignin… *except* money." We hope to help identify the technical barriers that need to be overcome to make lignin usage economically viable and thereby dispel this myth.

3 Overall Approach

The steps in the overall consideration for the analysis of lignin are depicted in the flow diagram below (Figure 2).

```
┌─────────────────────────────────┐
│ 1. Catalog potential materials  │
│    and chemical products from   │
│    lignin                       │
└─────────────────────────────────┘
                │
        ┌───────────────┐
        │ 2. Sort by    │
        │   product type│
        └───────────────┘
                │
        ◇ Three product types ◇ ──→ [ 3. Visualization of opportunities based on Product type ] ──→ [ Top opportunities diagram ]
                │
        ┌───────────────┐
        │ 4. Consider   │
        │  opportunity  │
        └───────────────┘
                │
        ◇ Near, Medium long term ◇ ──→ [ 5. Evaluation of technical barriers ] ──→ [ Barrier areas identified for R & D needs ]
```
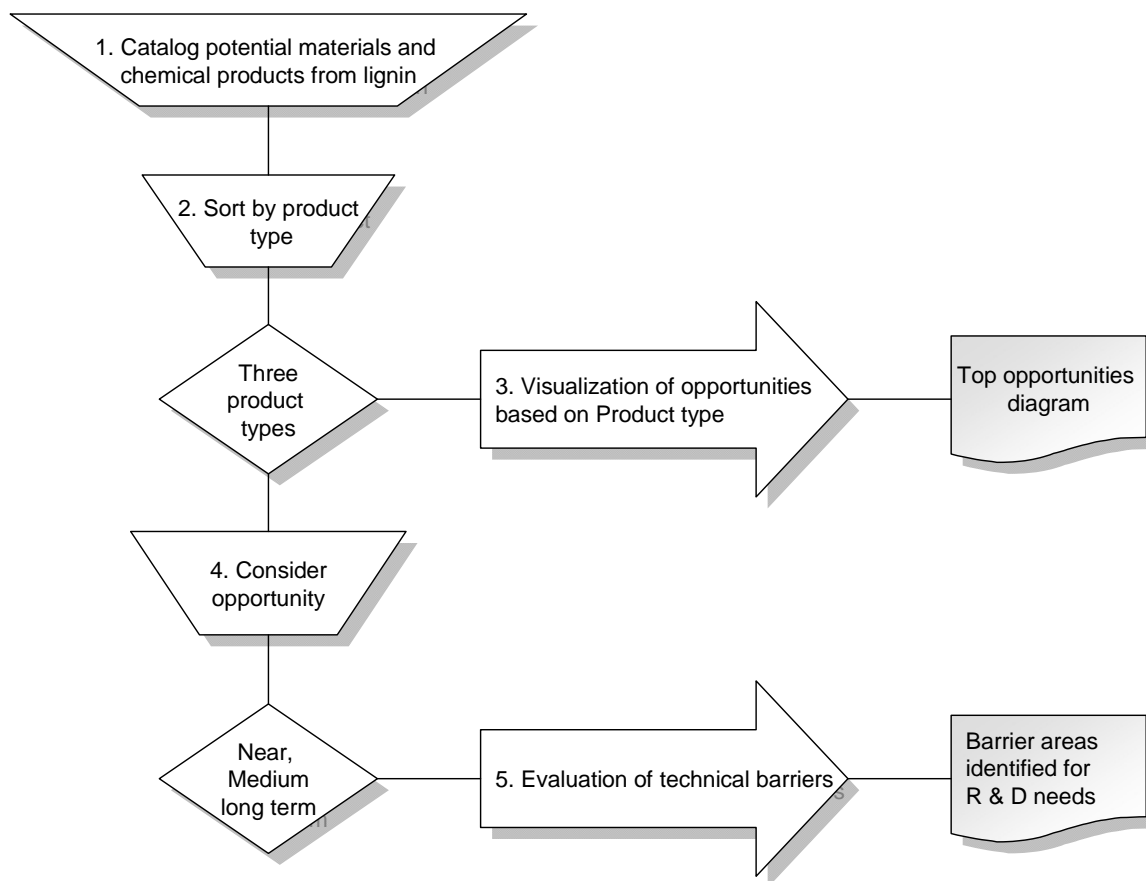
Figure 2 - Visual Representation of the Selection Strategy

Initially, a list of potential uses of lignin was assembled and compiled from various resources. Lignin-based opportunities could readily be divided into three categories: 1) power, green fuels, and syngas; 2) macromolecules; and 3) aromatics and other chemicals. The first category represents the use of lignin purely as a carbon source using aggressive means to break down its polymeric structure. The second category is the opposite extreme and seeks to take advantage of the macromolecular structure imparted by nature in high-molecular weight applications. Somewhere between the two extremes come technologies that would break up lignin's macromolecular structure but maintain the aromatic nature of the building block molecules, the third category. This is intriguing because lignin represents a potential starting source for the roughly 45 billion-pound domestic, non fuel, aromatic supply chain.

Once categorized, opportunities for the products in each category were considered. In the first category we included green fuels. These are described as liquid fuels that look like the fuels used today but are derived from biomass rather than petroleum. These differ from bio-derived ethanol and biodiesel in that green fuels need not be based on single alcohol or fatty acid methyl esters (biodiesel). The other categories are aimed at producing materials or chemicals rather than power or fuel, although the line can become somewhat blurred.

The opportunity for each category was then considered. Our evaluation included economics, the state of the current technology, and how the products would fit into the current and future infrastructure of the biorefinery and the chemical or fuel markets. Out of this consideration near-, medium and long-term opportunities were identified. The concept of near-, medium- and long-term opportunities corresponds with probabilities for lignin's value use in the biorefinery. "Near-term" is defined as current uses and those that seem possible within three to ten years. Some technology development will be required but much can be borrowed from currently available processes; for example, pyrolysis and syngas. "Medium-term" means five to perhaps 20 years out and requires significant technology development and some new fundamental knowledge; for example. use of lignin in high-molecular weight applications. "Long-term" means beyond ten years and requires significant new fundamental knowledge and significant new technology development; for example, direct catalytic conversion of lignin to gasoline type fuels or aromatic chemicals.

4 Lignin and Its Impact on the Biorefinery

Lignin

Since many in the chemical industry are not familiar with lignin we offer a brief definition here. Lignin, from Latin meaning wood, is a natural amorphous polymer. It acts as the essential glue that gives plants their structural integrity. Of the three major natural polymers that make up ordinary plants—cellulose, lignin and hemicellulose—lignin is the second most abundant and the only biomass constituent based on aromatic units. There are several lignin reviews and monographs that cover various aspects of lignin structure.[2,3,4,5]

The structure of lignin is complex and changes according to biomass source and isolation technique and thus chemical modification to a selective product is going to be difficult. However, modification to a certain family of products is more likely. An overview of lignin structure is given in Appendix 2. Exemplary structural motifs found in softwood are shown in Figure 3.[6]

Lignin is composed of phenylpropenyl (C9)—randomly branched units. The phenylpropenyl building blocks, guaiacols and syringols, are connected through carbon-carbon and carbon-oxygen (ether) bonds. Trifunctionally linked units provide numerous branching sites and alternate ring units. Nature produces lignin by the enzymatic dehydrogenative polymerization of coniferyl alcohol (common in softwoods), syringyl alcohol (common in hardwoods) and coumaryl alcohol (common in grasses). More detail about lignin structure by source and the various linkages present in lignin can be found in Appendices 2 and 3. Understanding these linkage units may be helpful when considering chemistries, products, and technical barriers in creating value from lignin.

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[2] Lignin: Historical, Biological and Materials Perspectives, Glasser, W. G.; Northey, R. A.; Schultz, T. P. Eds.; ACS Symposium Series 742, American Chemical Society, Washington, DC, 1999.

[3] Lignin Properties and Materials, Glasser, W. G.; Sarkanen, S. Eds.; ACS Symposium Series 397, American Chemical Society, Washington, DC, 1988.

[4] Lebo, S. E. Jr.; Gargulak, J. D.; McNally, T. J. Lignin. Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition [Online]. John Wiley & Sons, Inc. 2001. DOI: 10.1002/0471238961.12090714120914.a01.pub2.

[5] Nimz, H. H. Ullmann's Encyclopedia of Industrial Technology, Wiley-VCH Verlag GmbH&Co. KGaA.

[6] URL http://www.helsink.fi/orgkm_ww/lignin_structure.html
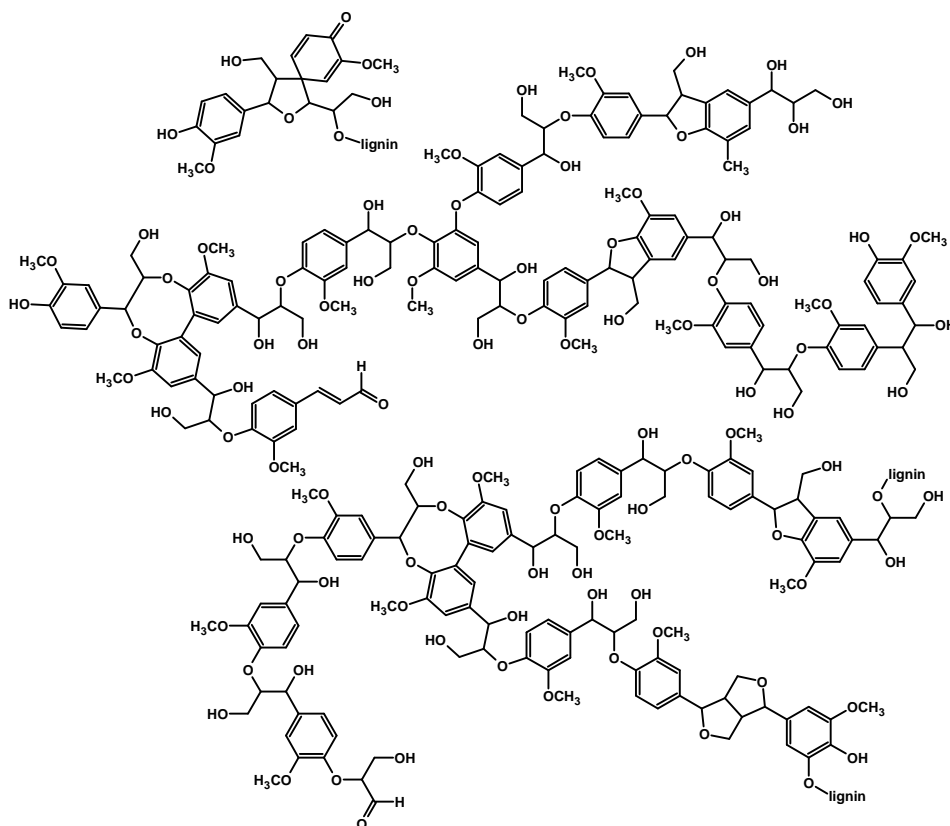
Figure 3 - Structural Motifs of Softwood Lignin

How Lignin Can Impact the Biorefinery

Lignin offers a significant opportunity for enhancing the operation of a lignocellulosic biorefinery. It is an extremely abundant raw material contributing as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass. Lignin's native structure suggests that it could play a central role as a new chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals.

DOE recently completed a study that suggests 1.3 billion tons of biomass is available annually in the United States.[7] This amount of biomass could potentially produce 130 billion gallons of liquid transportation fuels (ethanol, mixed alcohols, green gasoline, biodiesel and green diesel). Significant new technology developments are needed to maximize production and capture the resources. Interestingly, the same resource is sufficient in size to supply virtually all of the raw materials now required for the chemical industry.

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[7] "Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply" available electronically at http://www.osti.gov/bridge (ORNL/TM/-2005/66)

DOE, at the request of the President, has set a goal of twenty percent reduction of gasoline in ten years.[8] Five percent of the reduction is to be met by fuel efficiency with the remainder coming from alternative fuels. This equates to the production of 35 billion gallons of liquid transportation fuels by 2017. By 2030 the target is to replace thirty percent of the transportation fuel supply with biofuels,[9] which equates to roughly 60 billion gallons. Production of 60 billion gallons of ethanol, or other bio-derived fuel, would require the use of approximately 0.75 billion tons of biomass (1.5 billion pounds). The resultant lignin produced would be about 0.225 billion tons. The lignin could be used to produce power, liquid transportation fuels or products. Distribution of these three options depends on many factors including biomass source, regional location and available technologies. Of the three, only heat and power production are fully demonstrated today.

An approach that only considers process heat would be shortsighted. Higher value products present economic opportunities. Lignin could have a significant impact on increasing the amount of liquid transportation fuel available from biomass over the carbohydrate fraction alone by up to twenty percent.[10] In Appendix 1 we consider six scenarios where 0.225 billion tons of lignin are utilized for power, transportation fuels, products and various combinations of the above. When lignin is used for purposes other than power the overall revenue improvement is $12 to $35 billion. This is a significant value improvement not to be overlooked. However, as will be shown in this report, significant technology development will be required to capture the value benefit.

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[8] 2007 State of the Union Address, 20 in 10: Strengthening America's Energy Security, http://www.whitehouse.gov/stateoftheunion/2007/initiatives/energy.html
[9] Biofuels initiative (BFI) 2006, see Office of the Biomass Program Multiyear Program Plan 2007-2012, http://www1.eere.energy.gov/biomass/pdfs/mypp.pdf
[10] See Appendix 1 for six scenarios that consider the use of lignin for power, transportation fuels and chemical products.

5 Initial Screening of Opportunities from Lignin

We considered many possibilities for products from lignin and the various real or theoretical technologies required to make lignin-derived products a reality in the biorefinery. Unlike the screening process used in Volume I, which focused on sugars, identifying products from lignin was more challenging because of lignin's complex nature as a feed. Often, rather than listing discrete chemicals, classes of chemicals were identified based on functionality. Nevertheless, more than 50 opportunities were catalogued.

The possible products were evaluated on the basis of a combination of fit with currently available technology for their use, likely acceptance in the products marketplace (known market or unknown market) and an assessment of the degree of difficulty to develop the technology. The compounds were scored as high, medium, or low using the following criteria:

- **Technology degree of difficulty** – this evaluation assessed the potential number of steps required and the relative difficulty of achieving those steps. For many of these compounds, there is little or no existing industrial experience or process evaluation history to draw on. The assessment for this criterion was made based on available information from the open literature, evaluation of the potential process by the team, and other experts as necessary.

- **Market** – this criterion evaluated both potential market size and expected product value using standard reference sources such as the *Chemical Economics Handbook*.

- **Market risk** – this criterion evaluated the potential risk of bringing a given lignin-derived product into the market. An example of a risk considered "low" would be the introduction of a lignin-based source of BTX or syngas. A risk considered "high" included compounds currently not recognized as chemical building blocks (i.e., eugenol) or products that would likely be produced as mixtures.

- **Building block utility** – this criterion assessed the potential of a candidate compound to serve as a starting material for a larger group of derivatives.

- **Mixture** – this criterion assessed whether a candidate could be derived from lignin as a single compound or whether it would be present as a complex mixture.

The analysis is shown in Table 1.

Table 1 – Products Potentially Derived from Lignin Conversions

Lignin Derived Product	Current Technology Status from Lignin*	Expected Difficulty from Lignin*	Market Volume*	Market Value†	Market Risk*	Utility as Building Block*	Expected from Lignin as Mixture?
Process Heat & Power	H	L		$6/10^6$ Btu	L	NA	NA
Syngas	H	L‡	H	Variable	L	H	NA
Syngas Products							
Methanol/Dimethyl ether (DME)	H	L	H	$0.80/gal	L	H or Fuel	Y
Ethanol/mixed alcohols	L	H	H	$1 - $3.5/gal	L - M	H or Fuel	Y
Fischer Tropsch Liquids	H	L	H	$1.5 - $2/gal	L - M	L	Y
Mixed Liquid Fuels	M	M	H	$1.3 - $2/gal	L	L	Y
By-product C1 to C7 gases, hydrocarbons, or oxygenates	L	M - H or as consequence of other transformations	NA	variable	L	Perhaps or use for reforming/ gasification	Y
Hydrocarbons							
BTX and Higher Alkylates	L - M	M		$2/gal	L	H	Y
Cyclohexane	L	M	H	$2.20/gal	L	M	Y
Styrenes	L	M-H	H	$0.70/lb	?	?	?
Biphenyls	L	H	L - M	?	?	L	Y?
Phenols							
Phenol	L-M	M	H	$0.55 - $0.65/lb	L	H	N
Substituted Phenols			M	$0.70 - $2.00/lb	M	M	Y
Catchols, cresols, resorcinols	L	H		>$1.5/lb	?	M	Y
Eugenol	L	H	?	M-H	?	?	Y

Table 1 – Products Potentially Reachable from Lignin Conversions (Continued)

Lignin Derived Product	Current Technology Status from Lignin*	Expected Difficulty from Lignin*	Market Volume*	Market Value[†]	Market Risk*	Utility as Building Block*	Expected from Lignin as Mixture?
Syringols	L	H	?	M-H	?	?	Y
Coniferols	L	H	?	M-H	?	?	Y
Guaiacols	L	H	?	M-H	?	?	Y
Oxidized Products							
Vanillin	H	L	L	$5.90/lb	H	L	N
Vanilic Acid	M	M	?	?	H	?	?
DMSO	H	L	M	<$1/lb	H	L	N
Aromatic Acids	L	H	H	$0.40 - $0.50/lb	L	H	Y
Aliphatic Acids	L	H	H	$0.45 - $0.65/lb	L	M-H	Y
Syringaldhyde and Aldehydes	L	H	?	?	M-H	M	Y
Quinones	L	H	L-M	> $1/lb	?	L	?
Cyclohexanol/al	L	H	H	> $0.75/lb	L	H	Y
Beta keto adipate			?	?	H	M	?
Macromolecuels							
Carbon Fiber	L - M	M - H	H	ACC Target *= $3 - $5/lb	M	L	N
Polyelectrolites	L - H	M	M	$1.5 - $3/lb	M-L	M	Y
Polymer Alloys	L - M	M	?	$1 - $2/lb	M	NA	Y
Fillers, Polymer Extender	M	H	M	< $1/lb	M - H	NA	Y
Substituted Lignins							
Carbonylated	L	H	?	?	M - H	?	Y
Ethoxylated	L	M	L	$1.50 – 2.50	M - H	?	Y
Carboxylated	L	M	L	$1.50 – 2.50	M - H	?	Y
Epoxidized	L	H	?	?	M - H	?	Y

Table 1 – Products Potentially Reachable from lignin (Continued)

Lignin Derived Product	Current Technology Status from Lignin*	Expected Difficulty from Lignin*	Market Volume*	Market Value†	Market Risk*	Utility as Building Block*	Expected from Lignin as Mixture?
Esterified (Acetoxy)	L	H	?	?	M - H	?	Y
Thermosets	L	H	?	?	M	N	Y
Composites	L - M	M - H	?	?	M	N	Y
Formaldehyde-free Adhesives and Binders	L - M	M - H	H	Dependant on Regultory Environment	M - H	N	Y
Wood Preservatives	L	H	M	M	?	N	Y
Nutraceuticals/Drugs	L	H - M	H	H	H	N	Y
Mixed Aromatic Polyols	L	H	?	?	M	?	Y

* H = High or Well Developed
  M = Moderate or Partial development
  L = Low, or Emerging, Requires Intensive Effort for Development
  ? = Unknown or insufficient information
  NA = Not Applicable

† Prices are 2005 or mid-2006 where available

‡ Gasification technology is dependent on lignin source and in some cases the technical feasibility can be high, for example gasifying black liquor will have a different set of difficulties than other lignin containing fractions.

Downselecting

A ready downselection occurred as the product opportunities readily fit into one of three categories:

- power, fuel and syngas
- macromolecules
- aromatics and miscellaneous monomers

Specific types of products can arise with suitable technology development from each of these classes. The categories themselves fit into near-, medium- and long-term opportunities.

- Near-term: power, fuel and syngas
- Medium-term: macromolecules
- Long-term: aromatics and miscellaneous monomers

Each of the categories is discussed individually in the chapters that follow. Each category includes information on the technology used, product examples that can be produced and the technical barriers (opportunities) that need to be overcome. Identifying and addressing the overarching technical barriers identified in this report provides a basis for potential DOE research to support the biorefinery.

6 Power—Green Fuels—Syngas

The immediate near-term opportunities for lignocellulosic biorefineries use lignin for process heat, power and steam. However, there are other opportunities to consider for lignin that could be implemented in the three to ten year time frame. Although these opportunities have technical challenges, they have few technology barriers, and R&D support can be largely limited to process engineering, recovery and integration refinements.

Combustion

Lignin combustion is practiced today in paper mills to produce process heat, power, steam and to recover pulping chemicals. For lignocellulosic biorefineries there will be technical challenges around material handling and overall heat balance and integration. These are engineering problems that are likely to be readily resolved by process engineering firms and equipment suppliers. DOE funding in this area is probably not necessary.

Gasification

Lignin gasification produces syngas (carbon monoxide/hydrogen); the addition of a second step employing water-gas-shift (WGS) technology allows production of a "pure" hydrogen stream with co-formation of carbon dioxide. Hydrogen can be used to make electricity (fuel cell applications) or for hydrogenation /hydrogenolysis. Syngas can be used in different ways. Technology to produce methanol/dimethyl ether (DME) is well established. The products can be used directly or may be converted to green gasolines via the methanol to gasoline (MTG) process or to olefins via the methanol to olefins (MTO) process. Because of the high degree of technology development in methanol/DME catalysts and processes this use of lignin-derived syngas could be readily implemented. The technology needs include the economic purification of syngas and demonstration that gasification can proceed smoothly with biorefinery lignin.

Fischer-Tropsch (FT) technology to produce green diesel represents another use of lignin-derived syngas. FT processes are well established. For example, Sasol has extensive technology in this area. The technical needs for FT include economical purification of syngas streams and catalyst and process improvements to reduce unwanted products such as methane and higher molecular weight products such as waxes.

The conversion of syngas to mixed alcohols has not been commercialized. It would allow the production of ethanol and other fuel alcohols or higher value alcohol chemicals. A major challenge for this technology is catalyst and

process improvements to increase space time yields[11] (catalysts are lacking in selectivity and rate). This would include reducing methane, reducing methanol, a three to five time increase in the yield of 2-carbon and higher alcohols.

Although syngas production via gasification is a well developed technology for coal (and natural gas), there is continuing controversy over gasification economics at the scale anticipated for the lignocellulosic biorefinery. The economics of gasification improve with increasing scale and it is not clear that processing 2000 to 6000 dry tons per day will be economical. Thus, a better understanding of this issue is needed and may lead to identification of specific improvements needed in overall gasification technology. Gasification of different lignin sources may also differ. For example gasification of black liquor, a byproduct of pulping, has been problematic within industry.[12]

Gasification may fit into a biorefinery in numerous ways. Two examples are shown in Figures 4 and 5. In the first example, the gasifier could be a stand-alone process (Figure 4). Biomass residues would be fed directly into the gasifier. The resultant syngas would then be converted to products such as FT liquids (including green fuels), methanol or mixed alcohols.
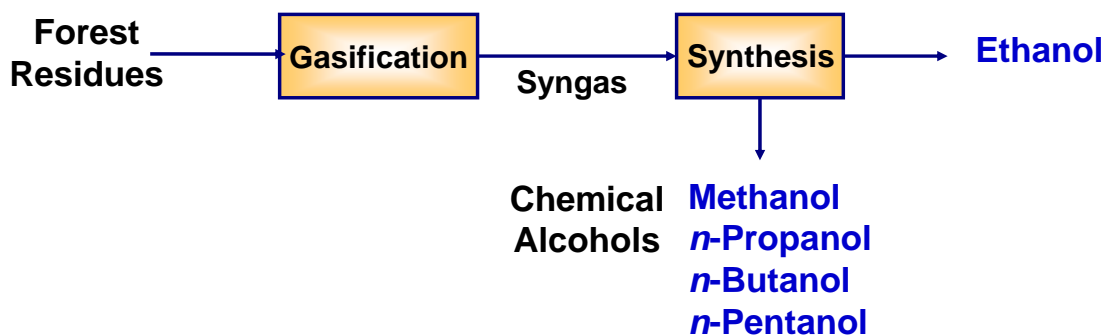
Figure 4 - Thermochemical Stand-Alone Gasifier

In the second example, the gasifier is integrated into a biochemical lignocellulosics biorefinery (Figure 5). In this biochemical/thermochemical integrated biorefinery the lignin-rich residue from lignocellulosics are fed into the gasifier. Sugars are primarily converted into ethanol while the lignin is primarily converted into syngas products.

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[11] Space time yield = kg of product/kg of catalyst/h.
[12] JEH personal correspondence with Weyerhaeuser
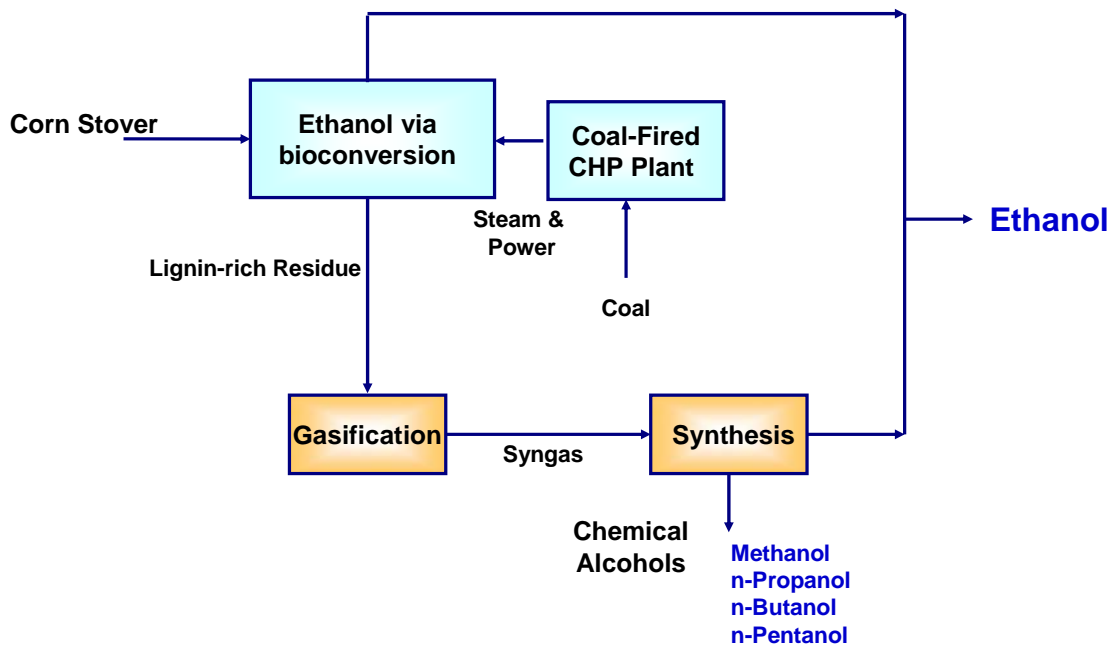
Figure 5 – Biochemical/Thermochemical Integrated Refinery

Pyrolysis

Fast Pyrolysis is a method that can convert dry biomass to a liquid product known as pyrolysis oil or bio-oil. As produced, bio-oils are generally quite unstable to viscosity changes and oxidation, which makes their use for chemicals and fuels problematic. Pyrolysis oils could be incorporated into certain petroleum refinery processes provided they are appropriately pre-treated and stabilized. The outcome would be displacement of a fraction of imported petroleum and the production of green fuels and chemicals. Technology needs include 1) preconditioning the pyrolysis oil before stabilization, 2) catalyst and process development to stabilize the pyrolysis oil for storage and transport from a biorefinery to a petroleum refinery; and 3) validation of the stabilized pyrolysis oil compatibility with current petroleum conversion catalysts and processes. For each of the three catalysts, lifetime remains an issue.

As for gasification technology, pyrolysis technology could be the basis for a stand-alone biorefinery (Figure 6) or integrated into a biochemical/thermochemical refinery (Figure 7). The water-soluble portion resulting from pyrolysis could be gasified to produce syngas or treated catalytically to produce methane for power.[13]

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[13] DOE has developed technology through PNNL to convert residues to methane-rich fuel gases. See Appendix 4.
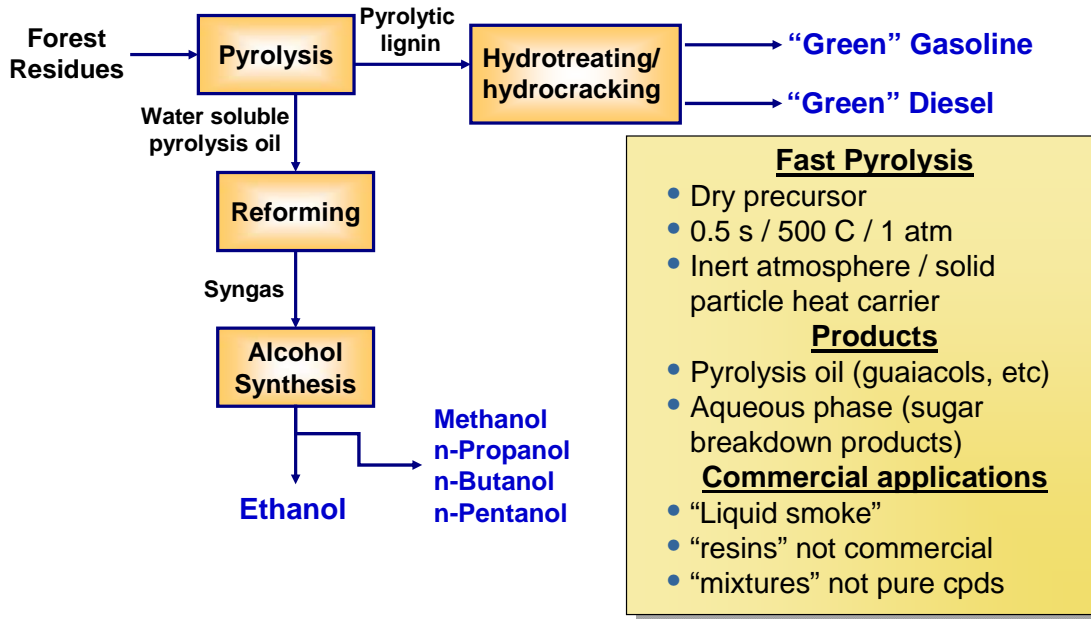
Figure 6 - Pyrolysis Integrated with Gasification
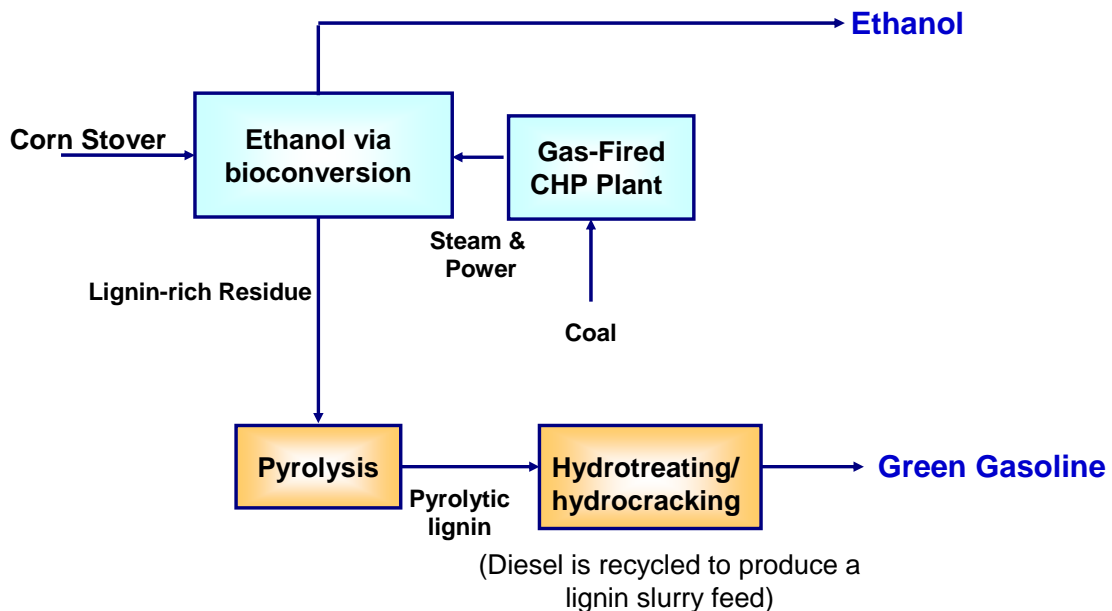
Figure 7 - Biochemical/Thermochemical Pyrolysis Biorefinery

Hydroliquefication

Lignin can also be converted into reformulated gasolines as a near- to medium- term opportunity. UOP in 1988 patented some catalytic technology in this area.[14] Hydrocarbon Research Inc. also has done work that incorporated lignin feeds into their proprietary H-Oil™ hydroliquefaction process.[15] In collaboration with the University of Utah, the National Renewable Energy Laboratory (NREL) has developed a multi-step process to convert lignin into a branched aromatic hydrocarbon product that can be used as a blending component for reformulated gasoline (Figure 8).[16] The first step, base-catalyzed depolymerization, breaks the lignin polymer into phenolic intermediates that can be hydroprocessed into the final product. The second and third steps include hydrodeoxygenation and hydrocracking to give the final gasoline-blending component. The final product is a mixture of naphthenic and aromatic hydrocarbons. Samples of this final gasoline blending component have been produced at the liter-scale and tested as gasoline blends in spark-ignition engines. Further technical requirements include process demonstration at scale with appropriate feeds and demonstration of acceptable catalyst lifetimes. Technical challenges include combining process steps to improve overall economics. The fuels would need to be certified for consumer use and the overall process economics verified.
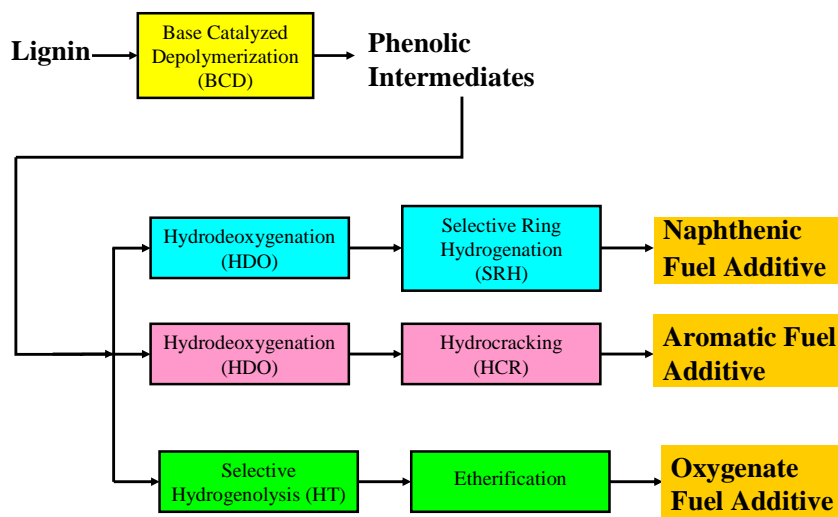
Figure 8 – Hydroliquification to Green Fuels and Oxygenates

[14] Urban; P.; Engel; D. J.; U.S. Patent 4,731,491 (to UOP) March 15, 1988.

[15] Huibers; D. T. A.; Parkhurst, Jr., H. J.; U.S. Patent 4,420,644 (to Hydrocarbon Research, Inc.) December 13, 1983. Naae; D. G.; Whittington; L. E.; Ledoux; W. A.; Debons; F. E.; U.S. Patent 4,787,454 (to Texaco) November 29, 1988.

[16] (a) Shabtai; J. S.; Zmierczak; W. W.; Chornet; E.; U.S. Patent 5,959,167 (to University of Utah) September 28, 1999. (b) Shabtai; J. S.; Zmierczak; W. W.; Chornet; E.; U.S. Patent 6,172,272 (to University of Utah) January 9, 2001. (c) Shabtai; J. S.; Zmierczak; W. W.; Chornet; E.; Johnson, D.; U.S. Patent Appl. 20030115792 (to NREL) June 26, 2003. (d) Shabtai; J. S.; Zmierczak; W. W.; Chornet; E.; Johnson, D.; U.S. Patent Appl. 20030100807 (to NREL) May 29, 2003.

Overview of Technology and Challenges

An overview of the technology, product examples and technical challenges for the Power—Green Fuels—Syngas product category is provided in Table 2.

Table 2 – Near-Term Conversion Technologies: Power—Green Fuels—Syngas

Technology	Product Examples	Technology Challenges
Lignin combustion	Process heat	Engineering and process integration
Gasification	MeOH/DME Green fuels olefins	Economic gas purification; process scale-up
Gasification	Fischer-Tropsch green fuels	Economic gas purification; catalyst and process improvements for methane and heavies reduction; process scale-up
Gasification	Fuel ethanol, propanol, butanol	Economic gas purification; catalyst and process improvements to produce 2-carbon and larger alcohols; process scale-up
Pyrolysis	Pyrolysis oil suitable for integration into petroleum refinery; process for green fuel and chemicals	Economical stabilization of pyrolysis oil for transport and compatibility in petro-refinery; process scale-up
Lignin fuels	Reformulated gasolines	Process demonstration; catalyst life; reducing number of process steps; process scale-up

7 Macromolecules

All current commercial uses of lignin, except combustion and production of synthetic vanillin and dimethylsulfoxide (DMSO), take advantage of lignin's polymer and polyelectrolyte properties. These are primarily applications targeted at dispersants, emulsifiers, binders, and sequestrants. In fact, nearly three-quarters of commercial lignin products are believed to lie within these applications. Other, smaller applications include adhesives and fillers. Generally, lignin is used in these applications with little or no modification other than sulfonation or thio hydroxymethylation. These uses mainly represent relatively low value and limited volume growth applications.

Lignin's commercial applications as a polyelectrolitic and polymeric material could be greatly expanded into higher valued macro monomer and polymer applications with the development of appropriate chemical and catalytic processes. This will require a better fundamental understanding of lignin reactivity relative to the source and the process by which it was isolated. This knowledge will help lead to development of appropriate technology to modify, control and amplify lignin's polyelectrolyte, chemical reactivity, including copolymerization, and compatibility properties with other monomers and polymers. A description of current commercial lignin use can be found in Appendix 6 and emerging lignin opportunities in Appendix 5; many of these include macromolecules.

Complete lignin depolymerization is an energy-negative process aimed at undoing what nature has done during biosynthesis. In the chemical and commercial lignin industry, one recurrent theme is that research is instead needed to enhance the uses and add value to the polymer that nature has already provided.

Examples of opportunities from macromolecules include: carbon fiber, polymer modifiers, adhesives and resins. One significant technical problem is that lignins from different biomass sources and isolation processes have significantly differing reactivity, molecular weight distributions, melting points and polyelectrolyte properties. These will be different in turn from the lignins recoverable from pulp mills. It is anticipated that R&D to develop appropriate lignin conditioning process technology will be necessary to alleviate the likely complications derived from these basic property and structural differences but will ultimately lead to new high-performance materials for the chemical and materials industries.

Carbon Fibers

Lignin represents a potential low-cost source of carbon suitable for displacing synthetic polymers such as polyacrylonitrile (PAN) in the production of carbon fiber (Figure 9).[17] Diverting ten percent of the lignin potentially available in the United States could produce enough carbon fiber to displace about half of the steel in

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[17] "Kline and Companies program for cost assessment of a new carbon manufacturing process" a final report to the Automotive Composites Consortium, March 29, 2004.

domestic passenger vehicles. Using lignin in the carbon fiber manufacturing process improves raw material availability, decreases raw material sensitivity to petroleum cost, and decreases environmental impacts. The goal of replacing steel panels with lightweight, yet strong, carbon fiber-reinforced plastics is to significantly reduce vehicle weight and improve fuel economy.

The initial step in economical lignin-derived carbon fiber production requires that lignin be melt-spun at high rates. The technical barriers in this step include low-cost purification of lignin to remove bound short lengths of polysaccharides, salts, particulate contaminants, water and other volatiles. Another technical challenge is dealing with lignin molecular weight polydispersity. Certain molecular weight fractions (either very high or very low) may need to be selectively removed. A final barrier is the development of practical new methods to process, stabilize and derivatize lignin and thus optimize its thermal (Tg), melt flow, and melting point properties. Another goal is to make lignin from different sources acceptable as a raw material for high-rate melt spinning and simultaneously capable of delivering high-carbon weight yields when the melt spun lignin fiber is thermally converted to carbon fiber.
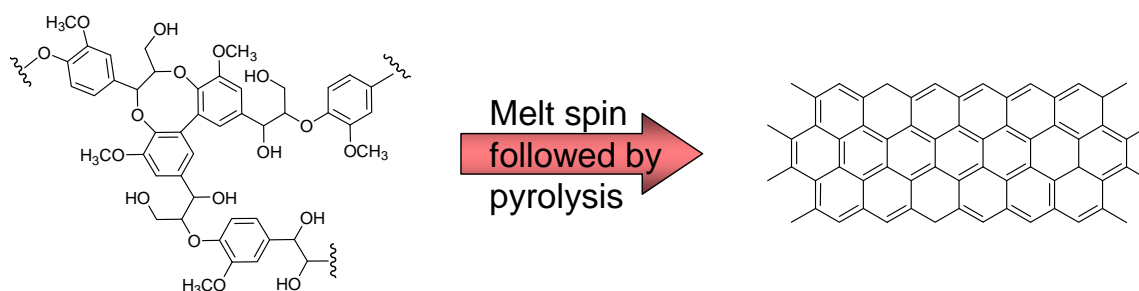
Figure 9 - Depiction of Low-Cost Carbon Fiber from Lignin

Polymer Modifiers

Polymer modifiers can be simple, low-cost fillers or may be high-value additives that improve various polymer physical or performance properties. Currently, lignin use concentrates on the former; future research should concentrate on the latter by creating technologies that improve polymer alloying, mutual solubility, cross-linking and control of color. Relevant technologies include predictable molecular weight control, facile introduction of reactive functionality and polyelectrolytic functionality. Examples of reactive functionality might include the addition of ethyoxy, epoxy, vinyl and carbonyl moieties. Molecular weight control could include polydispersity, depolymerization, molecular weight increase, intermolecular cross-linking or increasing phenolic functionality. The technical challenges surrounding polymer modifiers include understanding how to make these modifications economically, effectively and predictively with lignins of different sources. The modified lignins need to be validated in a variety of high-value applications. Applications may include high-strength engineering plastics, heat-resistant polymers, under-the-hood uses, antibacterial surfaces, high-strength and formaldehyde-free adhesives and

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light- and ultraviolet-resistant polymers. Another technology challenge for some of these applications is control of lignin color.

Resins/Adhesives/Binders

Resins and adhesives offer a large opportunity, especially for formaldehyde-free applications. Formaldehyde is currently considered a carcinogen and its banishment from consumer and packaging goods and building products is highly likely in the near term. The U.S. Department of Housing and Urban Development and the U.S. military are already moving in this direction. Technical needs and challenges for lignin in this area center on effective, practical means for molecular weight and viscosity control, functional group enhancement (for example, carbonylation, carboxylation, amination, epoxidation and de-etherification, that is, methoxy conversion to phenolic) to improve oxidative and thermal stability, provide consistent mechanical processing properties, control lignin color and provide precise control of cure kinetics. Product consistency in these application targets will also be a technical challenge.

Overview of Technology and Challenges

An overview of the technology, product examples and technical challenges for the macromolecules (high molecular weight) product category is provided in Table 3.

Table 3 - Medium-Term Conversion Technologies: High Molecular Weight Lignin Products and Classes Identified in the Evaluation

Compound or Class	Technologies Barriers/Needed Technologies
Carbon fiber	• Economical purified lignin sources • Economical modifications to allow high-melt spin rates • High carbon yields • Application to varied lignin sources
Polymer fillers	• Economical modifications to improve solubility and compatibility with other polymers • Controllable alteration of molecular weight • Control of polymer color • Control of polyelectrolyte character • Functional group enhancement
Thermoset resins Formaldehyde-free resins Adhesives and binders	• Molecular weight and viscosity control • Functional group enhancement (carbonylation, carboxylation, de-etherification) to improve oxidative stability, thermal stability, consistent lignin properties, cure rate consistency and lignin color

8 Aromatic Chemicals

Lignin is the only renewable source of an important and high-volume class of compounds—the aromatics. Demand for a few of the highest volume aromatics is shown in Table 4. It is easy to conclude that direct and efficient conversion of lignin to discrete molecules or classes of high-volume, low-molecular weight aromatic molecules is an attractive goal. As petroleum resources diminish and prices increase, this goal is very desirable, and is perhaps the most challenging and complex of the lignin technology barriers. Bringing high-volume aromatics efficiently from a material as structurally complex and diverse as lignin becomes a challenging but viable long-term opportunity.

Table 4 – Long-Term Conversion Technologies Required for Aromatics Market

Aromatic	U.S. demand (10^9 lb)	Lignin required* -theoretical- (10^9 lb)	Lignin required - current technology* (10^9 lb)
BTX	45.3	93	930
Phenol	5.09	10	80
Terephthalic acid	11.1	13	130
Total	**61.5**	**116**	**1,112**

*Theoretical lignin required is based on simple calculation of the relative molecular weights of lignin (taken to be 188 for organosolv lignin)[18] and the aromatic listed.[19] Using current technology, the best that can be achieved today is approximately ten percent of theoretical.

BTX Chemicals

When considering the different kinds of structural motifs present in lignin from various biomass sources, it is easy to conclude that technology developments may lead to two sets of compound classes.

One of these, which would arise from aggressive (i.e., non-selective) depolymerization in the form of C-C and C-O bond rupture, is aromatics in the form of BTX plus phenol and includes aliphatics in the form of C1 to C3 fractions (Figure 10). Of course, there is the possibility of forming some C6-C7 cycloaliphatics as

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[18] In comparison, kraft lignin has an average monomer molecular weight of 180 and lignosulfonate has an average molecular weight of 215-254. Lebo Jr., S. E.; Gargulak, J.E.; McNally, T. J.; Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition [online]. John Wiley & Sons, Inc.

[19] Terphthalic acid analysis likely underestimates the amount of lignin required on a theoretical basis as the carbon connectivity is not necessarily correct.

well. These products could be easily and directly used by conventional petrochemical processes (Figures 11 and 12). Development of the required aggressive and non-selective chemistries is part of the long-term opportunity but is likely to be achievable sooner than highly selective depolymerizations. In fact, some of the past hydroliquefaction work with lignin suggests that, with further development, this concept is a good possibility.
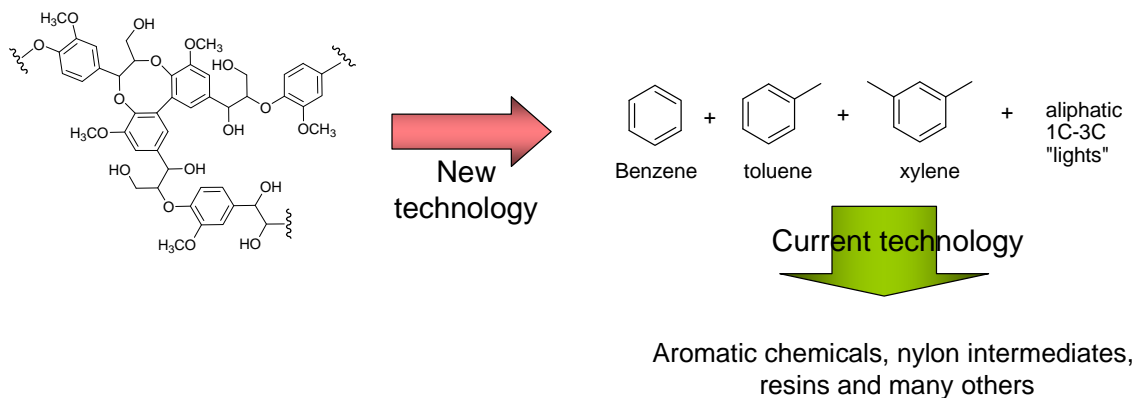
Figure 10 - Conversion of Lignin to BTX chemicals
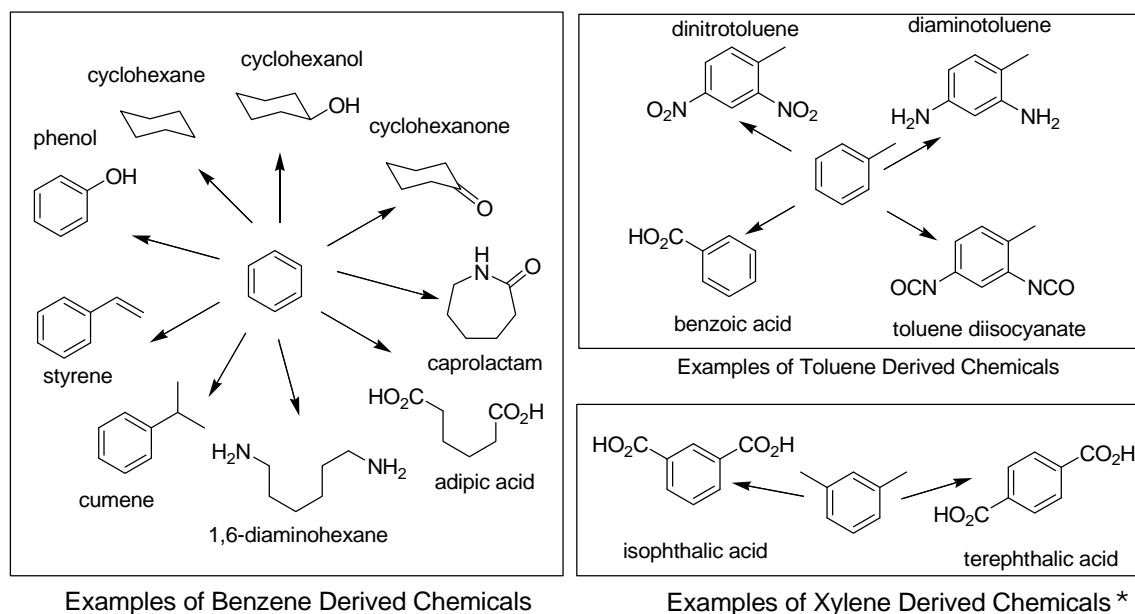
*Note the most likely form of xylene that can be produced from lignin is the meta isomer. However, isomerization of mixed xylenes to para-xylene is commercially done today and could provide para-xylene for the polyester markets.

Figure 11 – Examples of Current Technolgies Using BTX
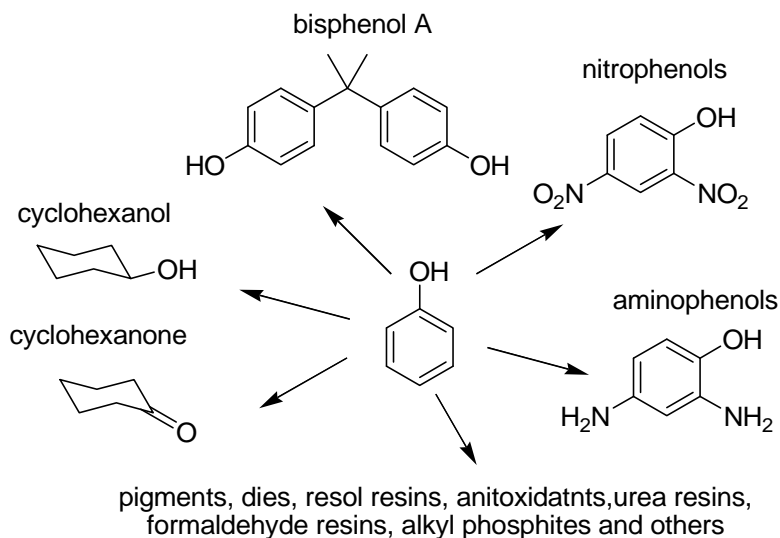
Figure 12 - Phenol Derivatives using Current Technology

Monomeric Lignin Molecules

Another view is that very selective depolymerization, also invoking C-C and C-O bond rupture, could yield a plethora of complex aromatics that are difficult to make via conventional petrochemical routes (Figure 13).[20] These compounds are closely related to the basic building blocks of lignin and may be highly desirable if they can be produced in reasonable commercial quantity. Two barriers would need to be overcome, however. First, technology would need to be developed that would allow highly selective bond-scission to capture the monomeric lignin building block structures. Development of this technology will be more difficult than the more aggressive processes that would yield BTX or phenols. Second, markets and applications for monomeric lignin building blocks would need to be developed. For the reasons listed above, this technology is longest-term and currently has unknown market pull for large-scale use. Since most of the chemical industry is used to single, pure-molecule raw materials, using mixtures of products in a chemical raw material feed, as would arise from lignin processing, constitutes a challenge. New/improved separation techniques for aromatic lignin monomers constitute a related challenge.

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[20] A current example is the production of lignin-derived vanillin.
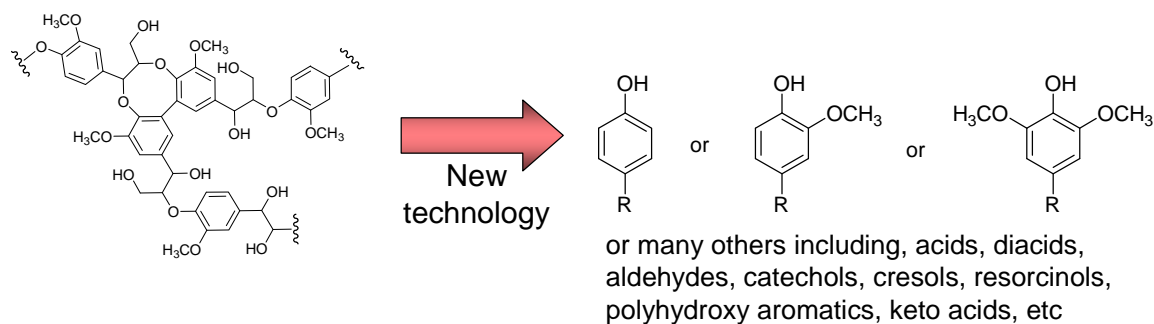
Figure 13 – Products that Preserve Lignin Monomer Structure

Low Molecular Weight Byproducts

In lignin processing, low-molecular weight aliphatics (C1-C3, etc.) also will be produced along with aromatics. Residual lights may include formic or acetic acids as well as aliphatics and olefins. Such low-molecular weight materials could be applied to syngas (reforming), alkylated gasoline or propane (LP) fuels. Alternatively, this material could be dehydrogenated to provide low-molecular weight olefins and residual lights. In a third option, the lights could be applied to power or heat production to provide the energy to drive the lignin conversion process.

Fermentation Products

Few fermentation routes are available today that use lignin as a nutrition source other than some routes that are of academic interest. In one such route, 2-keto-adipic acid is produced. Commercially viable fermentation technologies, possibly based on modifying "white-rot" fungi, represent a higher-risk area of research.

Overview of Technology and Challenges

An overview of the technology, product examples and technical challenges for the aromatics, including BTX, phenols, monomeric lignin molecules and other low molecular weight products is provided in Table 5.

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Table 5 – Long-Term Conversion Technologies: Aromatic Chemicals

Compound or Class	Technologies Barriers/ Needed Technologies
BTX Chemicals • Benzene • Toluene • Xylene	Catalysis – selective dehydroxylations and demethoxylations; dealkylations. Application of catalytic-reforming chemistry from petrochemical industry
Phenol	Catalysis – selective dehydroxylations and demethoxylations; hydrogenolysis; dealkylations. Application of catalytic reforming chemistry from petrochemical industry
Lignin monomer molecules (substituted coniferols) • Propylphenol • Eugenol • Syringols • Aryl ethers • Alkylated methyl aryl ethers	Catalysis – selective hydrogenolysis; formylation, hydrotreating, understanding of reactivity ratios, polymerization technology, formulations; catalytic dealkylation, demethoxylation, hydrolysis; control of side chain structure; controlled reduction, preservation of aromaticity; aromatic side chain cleavage, applications for mixtures; demethylation; ether cracking
Oxidized lignin monomers • Syringaldehyde • Vanillin • Vanillic Acid	Catalysis – selective oxidation
New Diacids and Aromatic diacids	Selective oxidations, catalysis, carbonylations, activation of ArOH bonds polymerization technology, formulation, understanding of polymer properties
β–Keto adipic acid, aliphatic acids, new Polyesters, new polyols	Biocatalysis; selective bioconversion of aromatics; selective oxidations-understanding of lignin peroxidases, laccases, etc.; polymerization technology, formulations; *P. Putida* transformations, development of new lignin converting organisms.
Aromatic polyols • Cresols • Catechols • Resorsinols	Catalytic hydroxylation processes, dehydrations, dealkoxylations, selective reductions, selective aromatic ring reduction technology
Cyclohexane and substituted cyclohexanes	Selective reductions and dealkylations
Quinones	Catalysis – selective oxidation (O_2, air, HOOH); radical-based oxidants; reactivity of phenolics and phenolic radicals

9 Challenges for Lignin Use within the Biorefinery

To this point we have identified opportunities and technology challenges—or barriers—for using lignin to form products. However, there are other technical challenges associated with the broader aspects of the lignocellulosic biorefinery operation. Biorefineries will be presented with different types and possibly changing mixtures of local biomass feedstocks. Depending on many factors, individual biorefineries may target different arrays of products in addition to fuels and thus use different, and possibly changing, biomass processing schemes. The inevitable result is a high degree of variability in the lignin recovered from different refineries.

Unique Nature of Lignin within Biomass

Lignin is unique among biomass components. It has an aromatic substructure. It does not act or react anything like carbohydrates or oils; it is more structurally and chemically complex. Carbohydrates may be separated from the parent biomass either intact—for later hydrolysis to monomeric carbohydrates—or directly as sugars. Oils are separated as triglycerides or as free fatty acids. In either case, processes for production of carbohydrate-derived chemical products via catalysis or fermentation deal with a fairly consistent and uniform feedstock largely independent of the recovery process.

Lignin, however, will come out of any biorefinery recovery process as a complex, polydisperse, high-molecular weight material with uncertain reactivity. This variability is the result of the different basic building block components that make up lignin, which depend on biomass source. The recovery processes used in any specific biorefinery will likely be chosen to optimize the carbohydrate stream and depend on many factors including biomass source and intended product slate. Depending on biomass source, the exact details of the biomass feed and the lignin recovery processes will result in lignins of differing, even changing, properties. This variability includes molecular weight distribution; isoelectric point; solubility; reactivity; number of free phenolic, hydroxyl and carboxyl groups; percent aromaticity; the types of aromatic substitutions (proton, hydroxyl, methoxy and alklyl); degree and type of cross linking; and amount of residual bound carbohydrate fragments.

Industrial lignins, especially those produced by conventional pulping processes, represent reactive feedstocks and will likely exhibit lower oxidative and thermal stability than other biorefinery process streams, depending on the conditions to which they are exposed. Time and temperature during storage and movement between unit operations likely will also influence lignin properties and reactivity.

Pyrolysis and gasification offer near-term solutions to the challenge presented by lignin variability. The discovery and development of economical processes that can retain lignin's inherent character for use in materials or chemicals is a longer-term

objective. The adaptation of such processes for diverse biomass sources will need to be demonstrated, otherwise lignins utility will be localized.

Lignin's variability, the presence of a large number of substructural units and its instability suggests that presenting lignin to any given process will likely result in a number of different reaction rates with reactions occurring at different sites. This will naturally lead to mixtures of products, for example mixed substituted aromatics, even if they are of similar nature.

This leads to another challenge for lignin use. The chemical industry is built largely on the use of uniform and consistent raw materials. It is unlikely that this will change, so technologies will need to be developed to precondition lignin to make its properties and reactivity patterns more stable, consistent, and uniform. One concept that may be of value is to separate lignin used for production of chemicals from the biomass early in biorefinery operations, using mild methods to conserve the structure. Developing and validating technology for this approach presents another challenge.

Choice of Lignin Separation Technology for the Biorefinery

Integrating a lignin process stream with the OBP's biochemical and thermochemical platforms will require identifying the best method to separate lignin from the biomass raw material cost-effectively. Although determining optimum lignin separation/isolation technologies for biorefineries is not the primary goal, it is an important parallel technical challenge. The structure, and in particular the reactivity, of a biorefinery lignin process stream will depend strongly on the method used for its separation. Moreover, each biorefinery will impose its own business model on the choice of lignin separation technology. Defining the best processes for a lignocellulosic biorefinery is well outside of the scope of this report.

This issue does lead to another need — that of sophisticated techno-economic analysis well suited to evaluating many different combinations of process scenarios and product combinations and determining the smallest subset that makes the most economic sense for any given biorefinery. The complexity of this question is illustrated by examining a forest-based biorefinery and the kraft process as a potential biorefinery lignin source. Kraft pulping is the dominant chemical pulping process and is described in further detail in Appendix 4.

From a current volume and infrastructure standpoint, kraft lignin is an attractive feedstock. Virtually all lignin process streams in today's domestic and world markets are the byproduct of kraft-based pulp and paper manufacture. The current process scenario for producing this lignin stream from forest biomass is shown in (Figure 14). However, in only a very few kraft mills worldwide is lignin separated for production of products. Only one of these units is in existence in the United States today.
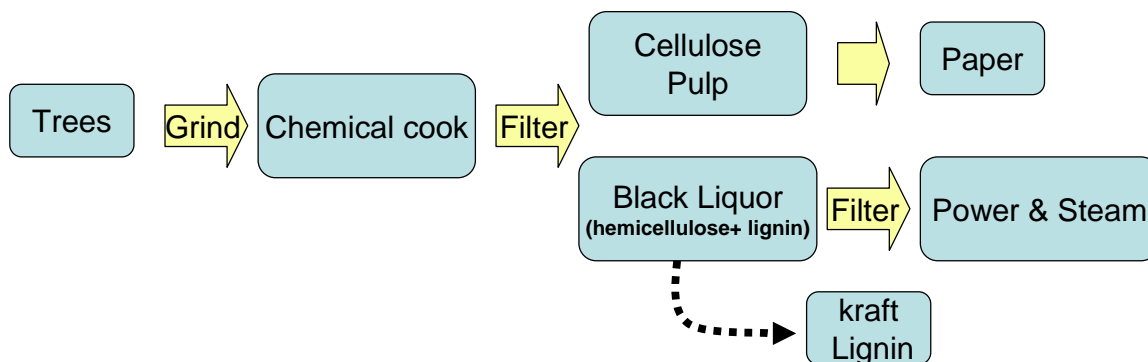
Figure 14 - Current Commercial Process Scenario for Lignin Use

The vast majority of lignin is not isolated in the kraft process but is used in the form of "black liquor" to supply the power, process steam and chemical recovery needs of the pulp mill. One option to increase the use of kraft lignin would be large-scale adoption of black liquor gasification by the pulp and paper industry. Black liquor gasification leads to more efficient power generation in a mill. The gas turbines associated with a gasifier are roughly twice as efficient as the steam turbines used in current chemical recovery processes. This increase in efficiency opens up a number of possible operating scenarios. For example, a biorefinery based on lignin gasification could tap into this increased efficiency by generating a higher proportion of its internal power needs. Alternatively, the biorefinery could generate the same amount of power and use excess syngas to produce higher-value products. Other scenarios that combine the use of existing chemical recovery processes with smaller gasifiers have also been suggested. Under these conditions, kraft separation of biomass raw material could allow lignin, via syngas in the thermochemical platform, to become a viable feedstock.

In contrast, the kraft process exhibits disadvantages, even with gasification included. These include its complexity, odor, expense, the significant effluents required and the large recycle volume for chemical handling and recovery. A further disadvantage of the kraft process is its inability to easily separate biomass into individual process streams of cellulose, hemicellulose and lignin. Kraft processing is not usually associated with non-wood feedstocks. Pulp mills also use changing mixes of tree types (softwood versus hardwood). The presence of sulfur in black liquor and in conventionally isolated kraft lignin also presents serious problems for any catalytic process.

In the future, biomass feedstocks will be expanded to include lignocellulosics from many sources including agricultural wastes or fast-growing trees. Processes will be needed to separate biomass (regardless of source) into its individual components. The carbohydrate fractions (cellulose and hemicellulose) will be broken down to simple sugars and used to produce liquid fuels and chemical products. Lignin would be available to provide power, syngas, high- and low-molecular weight products or liquid fuels (Figure 15). The choice of lignin separation processing and what fractions of the separated biomass components should be directed to various

products will be a decided on market and technical economic analysis. A discussion on this area is beyond the scope of this report and likely depends on many local or regional factors.
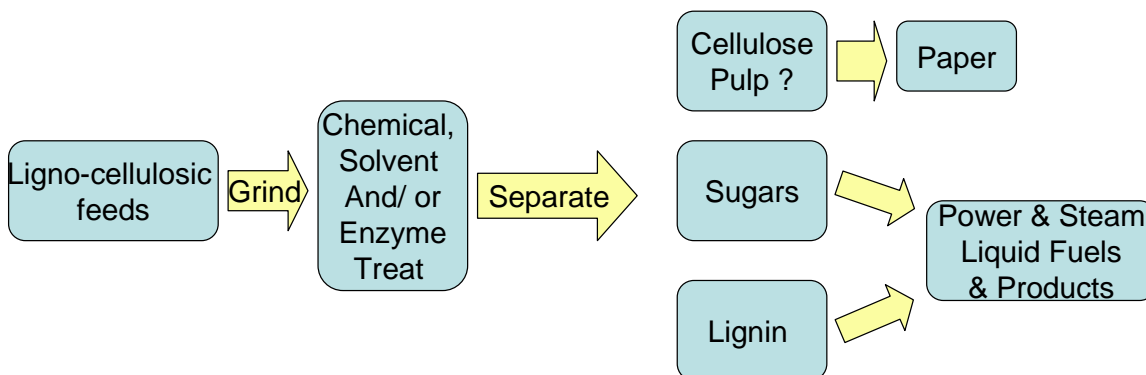
Figure 15 - Future Process Scenario for Biorefinery Lignin Use

Such questions are not unique to the kraft process. The R&D opportunities identified in this report have been chosen to help address and solve these issues. Every potential separation technique will need to be evaluated within several business and product scenarios. Ultimately, each biorefinery will need to choose a lignin isolation process, and perhaps also a conditioning process, that is most suitable for the products targeted.

As a biorefinery incorporates increasingly sophisticated technology for lignin transformations, it is likely that new sources of lignin will need to be incorporated. Table A.6 (Appendix 4) shows several separation technologies that produce a lignin byproduct stream and highlights the types of biomass for which they most likely apply. At the individual biorefinery level, it will be necessary to examine a range of potentially available lignin sources and lignin separation – isolation processes. It may be that several types may be optimally used in some biorefineries, and choosing these will likely become a techno-economic analysis issue.

Appendix 4 provides some detail for the diversity of lignin separation – isolation – recovery processes that could reasonably be incorporated into the biorefinery along with their advantages and disadvantages. Technology development in a lignin program combined with thorough techno-economic analysis would identify the sources and separation – recovery processes most likely to make the most impact within the biorefinery.

10 Moving Forward

The screening choices that led to the three most significant opportunities for lignin should be viewed as generic guidance. This report should next undergo brief industrial review. Reviewers from several industrial sectors have been selected. Through the review process the authors are looking for additional insight, collaboration or modification of the conclusions presented. In the meantime, the following seven points are recommended for moving forward.

Point 1. Lignin Utilization Offers Impact.

Lignin accounts for about 30% of the weight and 40% of the fuel value of biomass. Lignin, or lignin process residues, can always be used for process power through combustion. However, new opportunities afforded by technology development can lead to much higher overall value. In simple scenarios, an aggregate biorefinery industry that processes 0.75 billion tons of biomass could increase liquid fuel production by up to 12 billion gallons (an increase of 20%) and add $12 to $34 billion in revenues (Table A.1, in Appendix 1).

Point 2. R&D Offers a Balanced Portfolio.

As technology barriers are addressed, lignin transitions from a fuel source into a key biorefinery process stream. A portfolio of near-, medium- and long-term opportunities exists. In the near-term, gasification to syngas within the thermochemical platform or pyrolysis to bio oils can produce ethanol, mixed alcohols, green fuels or other syngas products. In the medium-term, opportunities that use lignin as a macromolecule for high-molecular weight applications exist. In the long-term, aromatic products with greater than a 60-billion-pound market remain a possibility.

Point 3. Technology is Available for Lignin Use Now.

Gasification processes can be used with almost any lignin process stream, regardless of source, making it ideal for near- to medium-term applications. Some medium-term opportunities also exist with macromolecules. Primary technical challenges to the use of lignin include the relatively small amount of R&D effort that has been expended toward developing lignin as a chemical feedstock, lignin's non-uniform structure, and choosing the best lignin separation/isolation process for the biorefinery.

Point 4. Aim DOE R&D Support at Technical Barriers.

The most effective investment of DOE funds will be in broadly applicable technology development. Medium- and longer-term opportunities will require transcending some significant barriers. This report has identified groups of provisional targets whose preparation would enable the development of needed lignin conversion

technology. These targets have been assessed with regard to their potential market impact. However, specific target molecules and applications are best defined by market pull factors identified by industry. One example barrier for lignin is the production of single products rather than mixtures. The chemical industry is not equipped to handle product mixtures in most of its processes. To address this barrier, new technology might be developed for product separations or to selectively remove specific linkages allowing control over product profile.

Point 5. Catalysis Will Be an Important Technology.

Highly developed and efficient catalytic processes are the essential key to today's petrochemical refinery. Efficient value maximization of the lignin stream within the biorefinery will be no different and requires catalytic processing. Thus, development of selective and robust catalytic processes specifically designed for lignin conversion must be a core effort in a biorefinery program. Selective oxidation, reduction, and bond breaking/making processes will be needed. Biochemical processes for selective lignin functionalization, or formation of selected structures, will be important. Catalytic processes leading to low-color lignin would facilitate its increased use in color-sensitive applications such as coatings, surfactants and polymer applications. This is a significant technical challenge that historically has played an important role in preventing large-scale industrial efforts to use lignin as a source of renewable carbon. However, the high-risk/high-reward nature of the challenge makes this effort ideal for work within the DOE Office of Biomass Program's national laboratories.

Point 6. Other Technology Support is also Required.

Maximizing the product opportunities from lignin requires that lignin separation technologies be improved or developed along with lignin utilization and product separation technologies. Because lignin has traditionally been relegated to use as a fuel, technologies complementary to lignin conversion have received less support. There is an R&D need to understand the chemical and structural features that result from various lignin separation/isolation processes. *Of highest importance is the need to remove lignin early and mildly in biomass fractionation processes.* Biomass fractionation processes designed to optimize the quality of the sugar stream almost always do so at the expense of the lignin stream. The longer lignin isolation is delayed, the more intractable it becomes. This report identifies several fractionation processes that give a useful lignin fraction while still maintaining a sugar stream of excellent quality (Appendix 4).

Lignin Conditioning
Subsequent to lignin isolation, further "lignin conditioning" steps may be needed to make it more amenable to further chemical transformation. These steps could include molecular weight reduction of the initially isolated lignin, choosing or chemically modifying lignin to favor certain functional groups, or selective separation of different molecular weight fractions. Developing technology to manage lignin's molecular weight could be of great importance in its development as a feedstock. Development of these types of processes for selective lignin

conversion could afford a much more tractable source of renewable carbon. The industry has learned how to convert equally complex materials (crude oil, coal) into useful building blocks. Technology tailored for the structural features of lignin should be able to accomplish the same goal, simplifying many of the proposed conversions in this report. It is also likely that the "conditioning" of lignin, that is, making it ready for conversion to building blocks and other products, also should be conducted as soon as possible after separation from its parent biomass.

Structure of Analysis

The analysis of lignin's structure has been ongoing for over a century. Yet surprisingly, a complete picture of lignin is still not available. The best chemical methods give high resolution, but only show the structure of the 30% of the lignin sample that is soluble. Spectroscopic techniques (e.g., near infrared) may give rapid information but only broad sketches of the true lignin structure. Parallel development of rapid, high-resolution processes (for example, recent developments in 2-D NMR) could greatly enhance our understanding of lignin structure, particularly for processed lignin.

Separation technology

Separation technology is always a component of conversion technology. However, it will be of special importance in a program directed at lignin conversion. Current lignin separation methods are directed mainly at optimizing the properties of the cellulose or sugar fraction of biomass and largely eliminating lignin. Advanced separation technology for lignin is needed both for upstream separation of lignin from biomass and downstream separation of lignin products from each other. Separation from biomass could include lignin recovery of different molecular weight ranges or isolation of a small group of low molecular weight lignin fragments.

While an ideal goal of technical development would be conversion of lignin to single compounds, lignin's heterogeneous structure will generally lead to product mixtures, perhaps enriched in a product of interest. Separation will be necessary to convert these mixtures into more useful product streams. Research into size-selective or functional group-selective processes will be important.

Point 7. Technoeconomic Analysis Should Guide Research

Technoeconomic tools can be used to guide research efforts by identifying where the most impact can be made. Lignin could become an equally important source of renewable carbon as sugar, but the research lags that of other biomass components. To effectively address the technical barriers in a reality of limited budgets, research must be carefully directed. R&D and analysis should work in parallel, supporting each other, to uncover opportunities in the shortest time.

Appendices

Appendix 1 – Increasing Revenue by Utilizing Lignin

Table A.1 shows the results of high level estimation of the revenue of lignocellulosic ethanol production under six scenarios. In each scenario the carbohydrate portion of biomass is converted to 60 billion gallons of ethanol. Lignin is used to produce power, syngas alcohols, aromatic chemicals (BTX), carbon fiber or combinations of the above. All calculations are based on an underlying assumption that 60 billion gallons of fermentation ethanol will require 0.75 billion tons of biomass and that biomass is composed of 30% lignin. Hence there will be 225 million tons (450 billion pounds) of lignin produced.

In Scenario 1 (base case) lignin is used for power. Under this scenario lignin provides a fuel credit value of $11.2 billion. This assumes that lignin has a fuel value of $0.04 per pound on a dry basis (Btu replacement with coal) but is discounted to $0.025 per pound as wet.

In Scenario 2 lignin is gasified and converted to mixed alcohols (syngas alcohols). The assumptions in this scenario are that one ton of lignin will yield fifty-five gallons of ethanol and 19 gallons of mixed alcohols (three to five carbon alcohols). The conversion involves gasification followed by catalytic upgrading of syngas. Although the fuel credit value is lost, the ethanol produced adds another $12.4 billion in revenue. The remaining mixed alcohols are valued at $2.55 per gallon and provide additional revenue of $12.1 billion. In addition to higher revenue, an additional 12.4 billion gallons of liquid fuel (ethanol) is produced in this scenario.

In Scenario 3, lignin is converted to simple aromatic chemicals (BTX). This assumes that lignin is converted at twenty weight percent efficiency, that one ton of BTX equates to 277 gallons and that BTX has a chemical value of $2.00 per gallon. Under this scenario 12.7 billion gallons of BTX are produced at a value of $24.9 billion. No effort is made to burn the 80% residual for power which would increase the overall revenue.

In Scenario 4, Lignin is converted to BTX with the byproducts (approximately 80% of the lignin) being gasified to provide syngas alcohols. The assumptions have been previously stated. In this scenario the revenue increases by $31.2 billion and ethanol production increases by 9.3 billion gallons.

In Scenario 5, lignin is converted to 11.7 billion pounds of carbon fiber – an amount that would go into 15 million cars (100 pounds of carbon fiber per car). The remaining lignin is gasified and converted to syngas alcohols. The carbon fiber production requires 1.5 billion pounds, less than one percent of

the lignin available. Carbon fiber is composed of 90% lignin and 10% synthetic polymer at an overall weight yield of 45%. The carbon fiber selling price is assumed at $3.50 per pound, although reasonable price structure could be $5 to $7 per pound. In this scenario the revenue increase is $16.1 billion and the increase in ethanol production is 11.7 billion gallons.

In Scenario 6, 1.5 million tons of lignin is converted to carbon fiber, the remainder is converted to BTX chemicals and the byproducts of that process are converted to syngas alcohols. In this scenario the revenue increase is $35 billion and an additional 8.6 billion gallons of ethanol are produced.

Note that increase in revenue does not necessarily mean an increase in profitability; that would assume the low cost processing of lignin. Identifying barriers to cost effective processing is the aim of this report.

Notes and assumptions for Table A.1:
1. Sixty billion gallons of fermentation ethanol requires 0.75 billion tons of biomass. If biomass is composed of 30% lignin that equates to 225 million tons (450 billion pounds) of lignin.
2. Lignin fuel value = $0.04/lb dry basis (Btu replacement with coal), but this is discounted to $0.025/lb as wet.
3. One ton of lignin yields 55 gallons of ethanol and 19 gallons of C3-C5 mixed alcohols when gasified and catalytically converted.
4. Mixed C3-C5 alcohols are valued at $2.55/gallon; BTX is valued at $2.00/gallon.
5. Lignin can be converted to BTX at a 20% weight efficiency; 1 ton BTX = 277 gallons.
6. Carbon fiber is composed of 90% lignin and 10% synthetic polymer with an overall 45% weight yield; selling price = $3.50 (could be as high as $5–$7/lb). For 15 million cars / year at 100 lbs carbon/car, the carbon fiber demand would be 1.5 billion lbs (requires 0.0015×10^9 tons of lignin or < 1% of the 0.225×10^9 available.
7. Added a five percent efficiency loss for syngas alcohols as a factor for the extra processing.
8. Added a ten percent efficiency loss for syngas alcohols as a factor for extra processing.

Table A.1 - Estimated Revenue Improvements Utilizing Lignin Produced from 60 Billion Gal of Ethanol

Lignin Product	Scenario 1 Power	Scenario 2 Syngas Alcohols	Scenario 3 BTX	Scenario 4 BTX + Syngas Alcohols	Scenario 5 Carbon Fiber + Syngas Alcohols	Scenario 6 Carbon Fiber + BTX + Syngas Alcohols
Notes and assumptions	1, 2	1,2,3,4	1,3,4,5	1,3,4,5,7	1,2,3,4,5,6,7	1,2,3,4,5,6,7?,8
Fuel Credit Value ($ billion)	11.2	- - -	- - -	- - -	- - -	- - -
Syngas EtOH (billion gal)	- - -	12.4	- - -	9.3	11.7	8.6
Value of EtOH ($ billion)	- - -	12.4	- - -	9.3	11.7	8.6
Increased EtOH production	- - -	20%	- - -	15%	20%	13.5%
Mixed Alcohols (billion gal)	- - -	4.3	- - -	3.2	4.1	3.0
Chemicals Value ($ billion)	- - -	10.9	- - -	8.2	10.4	7.6
BTX produced (billion gal)	- - -	- - -	12.7	12.5	- - -	12.4
BTX Value ($ billion)	- - -	- - -	24.9	24.9	- - -	24.8
Carbon Fiber (billion pounds)	- - -	- - -	- - -	- - -	1.5	1.5
Carbon Fiber Value ($ billion)	- - -	- - -	- - -	- - -	5.3	5.3
Revenue from lignin	11.2	23.3	24.9	42.4	27.3	46.2
Revenue Increase ($ billion)	- - -	12.1	13.7	31.2	16.1	35.0

Appendix 2 – Initial Evaluation of Lignin Opportunities

The evaluation process began by developing lists of broad opportunities for lignin conversion. The first output of this evaluation was a series of star diagrams for lignin conversion that was used to begin downselection of a large number of possibilities. This appendix summarizes the first lists of opportunities evaluated for the report. The intent of this activity was twofold: 1) generate a large number of hypothetical structures that might be available from lignin conversion, and 2) develop a preliminary list of conversion technologies.

Figures A.1 – A.6 suggest possible structures that could be derived from the guaiacyl and syringyl (see Appendix 3) units present in lignin. These applications have not been thoroughly investigated since only a few of the compounds in the figures were known to be commercially available in pure form and at low cost. In this early stage of evaluation, the structure used for lignin was strictly illustrative.
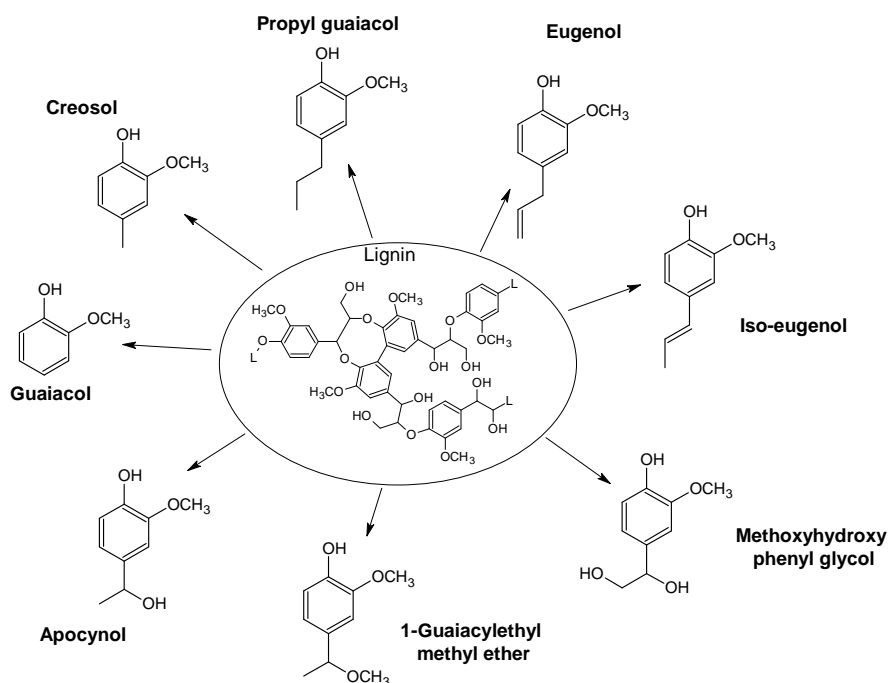
Figure A.1 - Potential Structures Available from Guaiacyl Units, Group 1
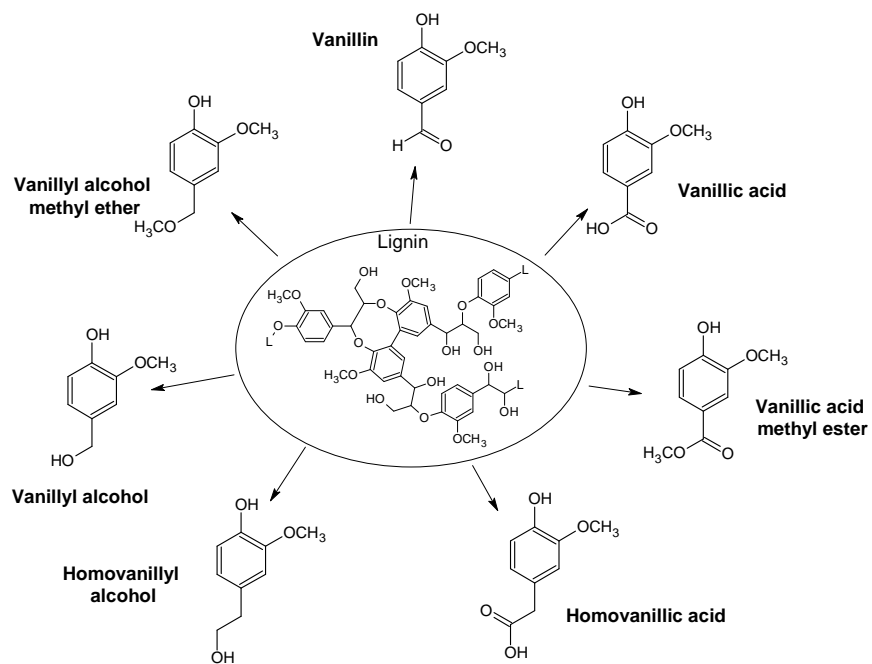
Figure A.2 - Potential Structures Available from Guaiacyl Units, Group 2
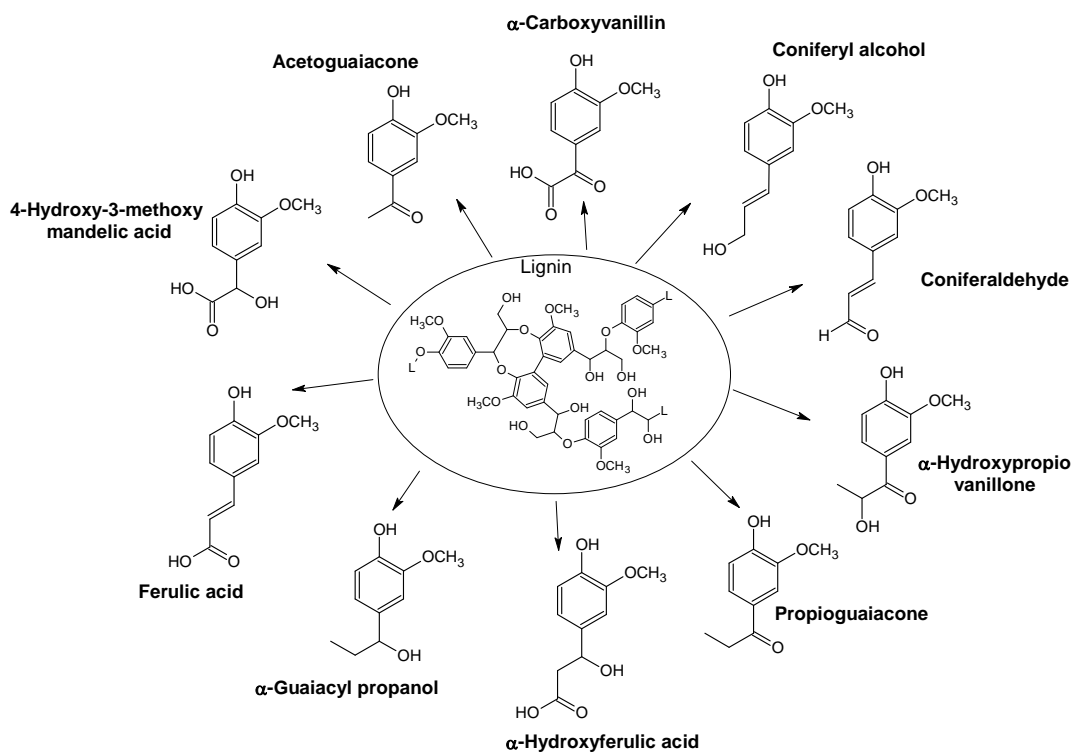
Figure A.3 - Potential Structures Available from Guaiacyl Units, Group 3
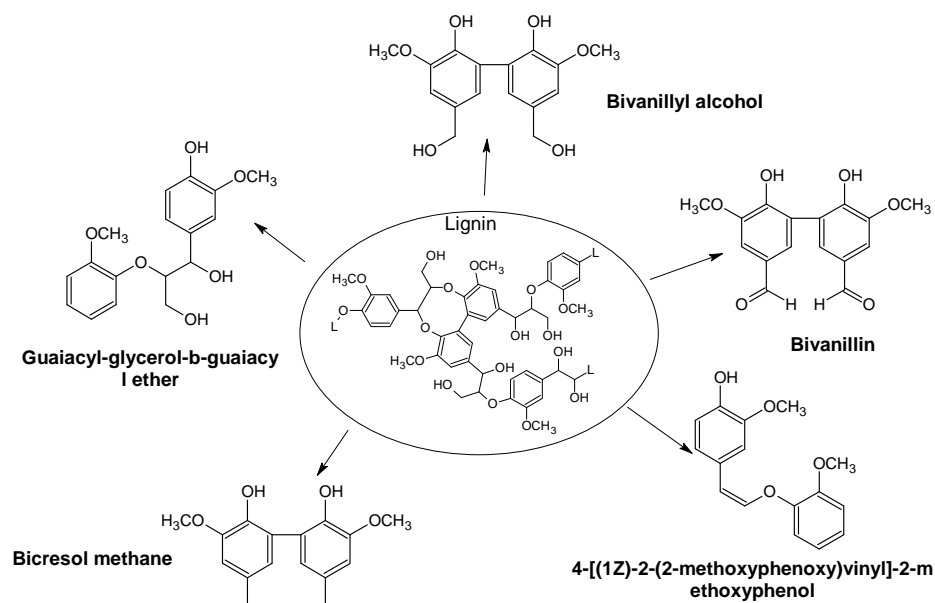
Figure A.4 - Potential Dimeric Structures Available from Guaiacyl Units, Group 1
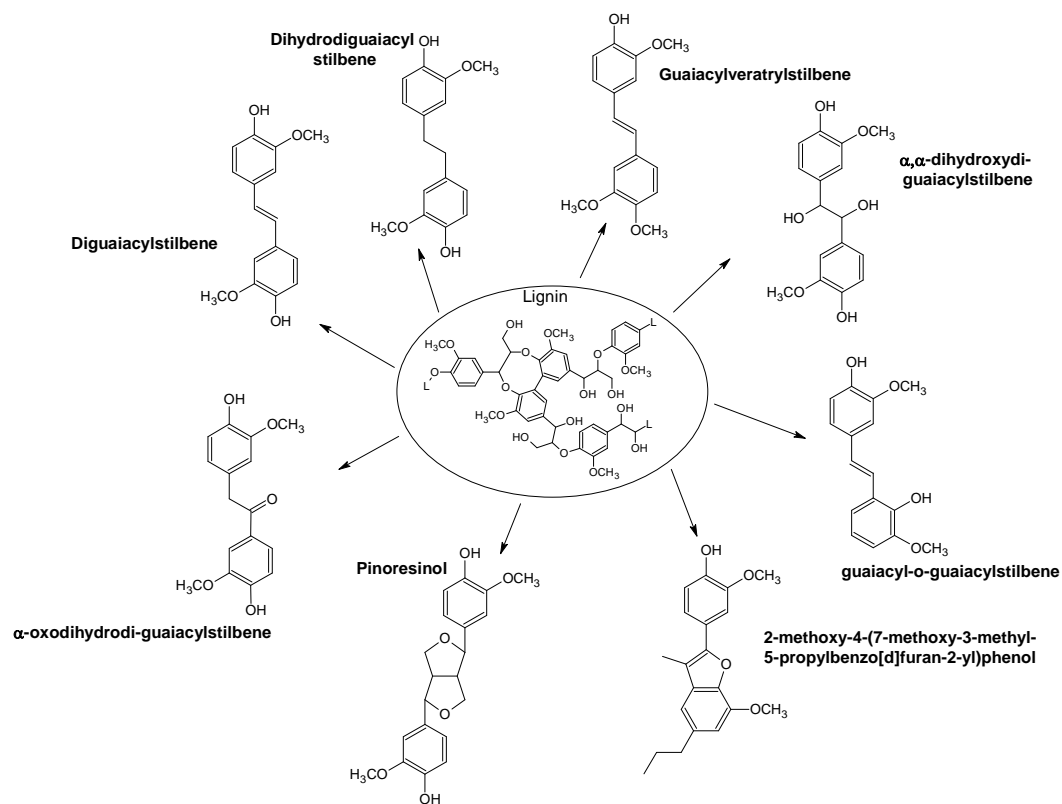
Figure A.5 - Potential Dimeric Structures Available from Guaiacyl Units, Group 2
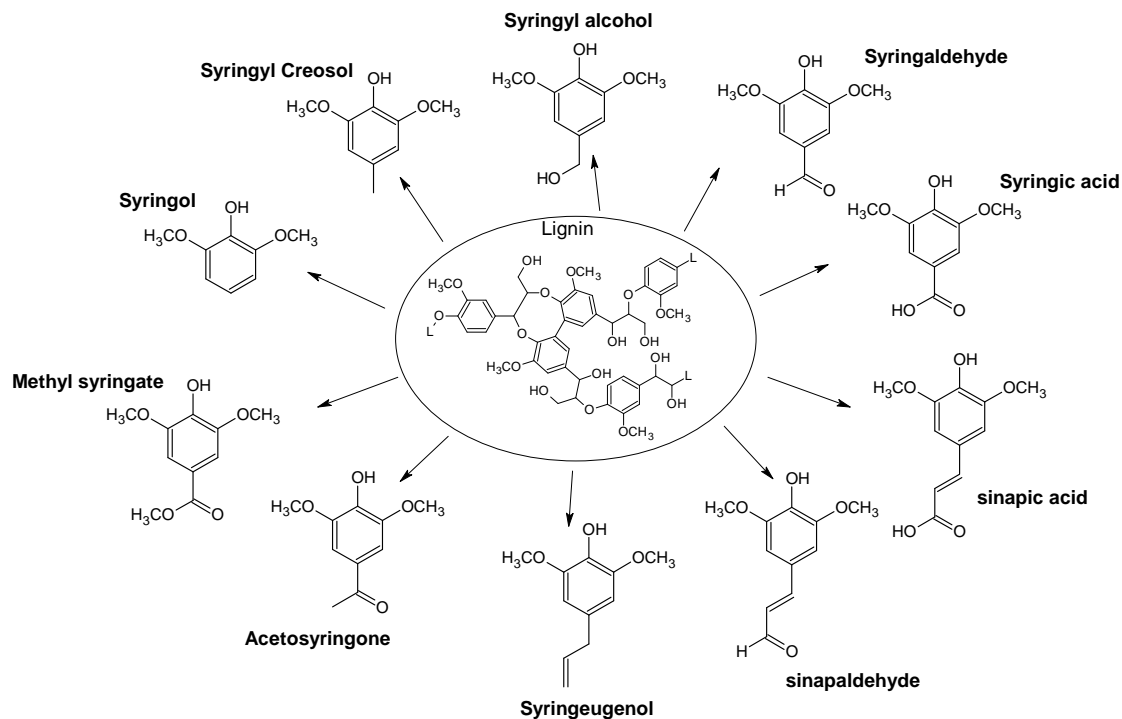
Figure A.6 - Potential Structures Available from Syringyl Units

Further evaluation examined lignin conversion to polymeric and other high-molecular weight molecules, for example, compounds available through lignin chain extension using propylene oxide or ethylene oxide (Figure A.7). Chain extension can significantly alter the physical property of lignin, even transforming solid kraft lignin into a wax or a viscous fluid.
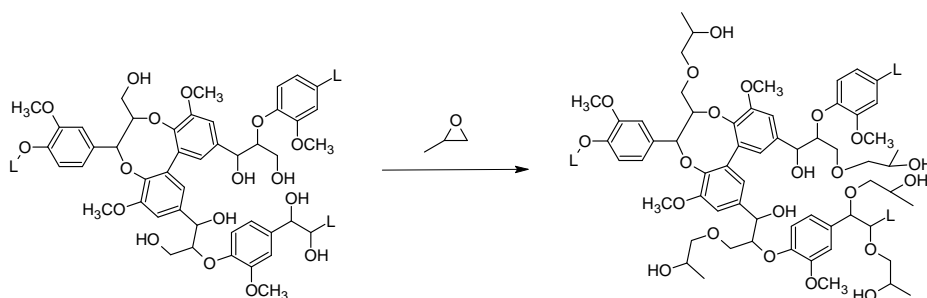
Figure A.7 - Conversion of a High-Molecular Weight Lignin Fragment to a Functionalized Macromonomer

Building from these diagrams, an initial list of possible lignin transformation technologies was developed (Figure A.8). These technologies were based on a review of literature conversions for lignin, and their potential application in biorefinery operations, and helped to identify the most important technologies for the final listing of opportunities materials.
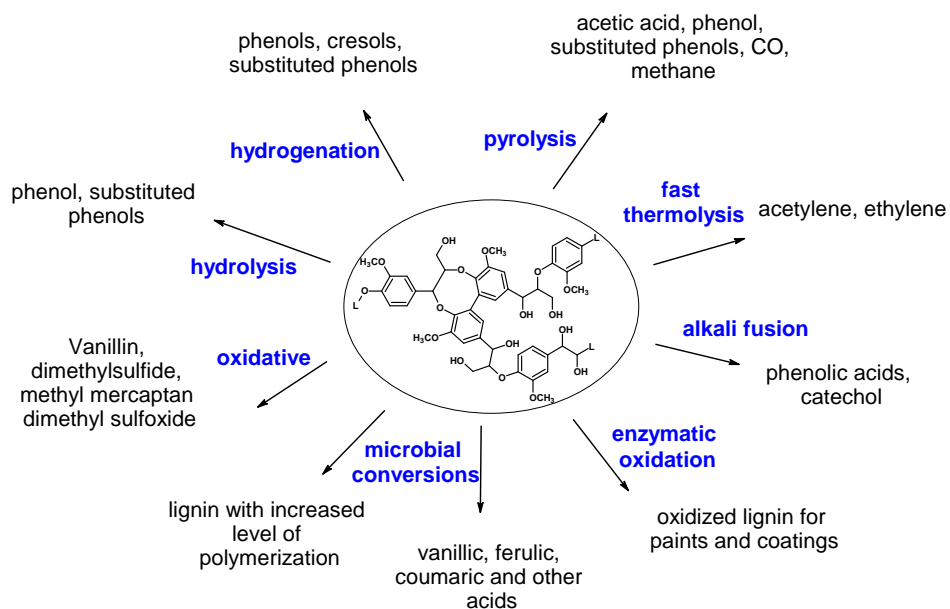
Figure A.8 - Brief Summary of Catalytic Lignin Transformations

In addition to evaluating conversions of new biorefinery lignin sources, an initial evaluation of conversion processes applicable to existing commercial lignin sources, such as lignosulfonates, was carried out (Figure A.9). Given lignosulfonate's central position within known lignin products, many of the markets shown in Figure A.9 were expansions of current uses; others represented new uses that would require further modification of the lignosulfonate polymer or alterations in lignin molecular weight. Both lignosulfonate and kraft lignin were found to offer potential utility in the chemical market, as summarized in Figure A.10.
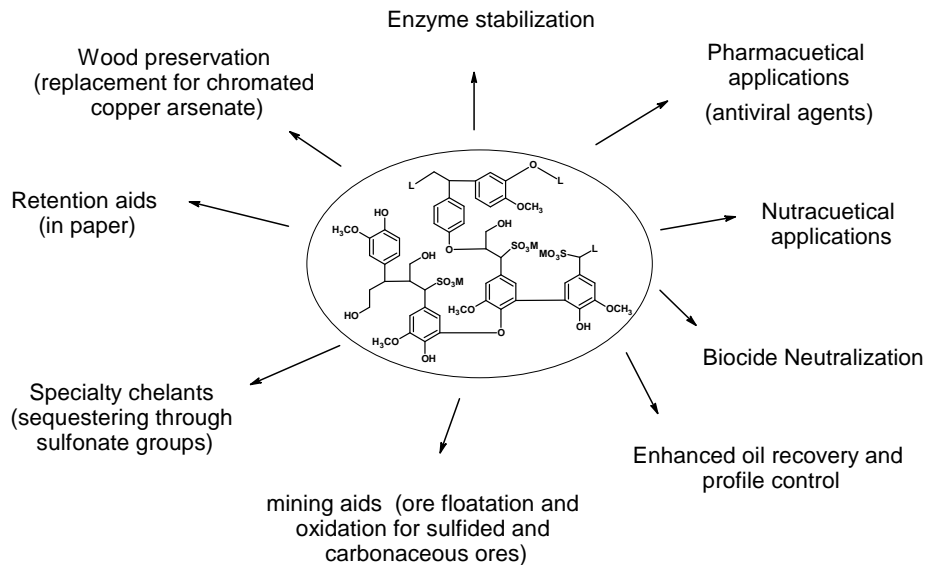
Figure A.9 - Potential New Products from Lignosulfonates
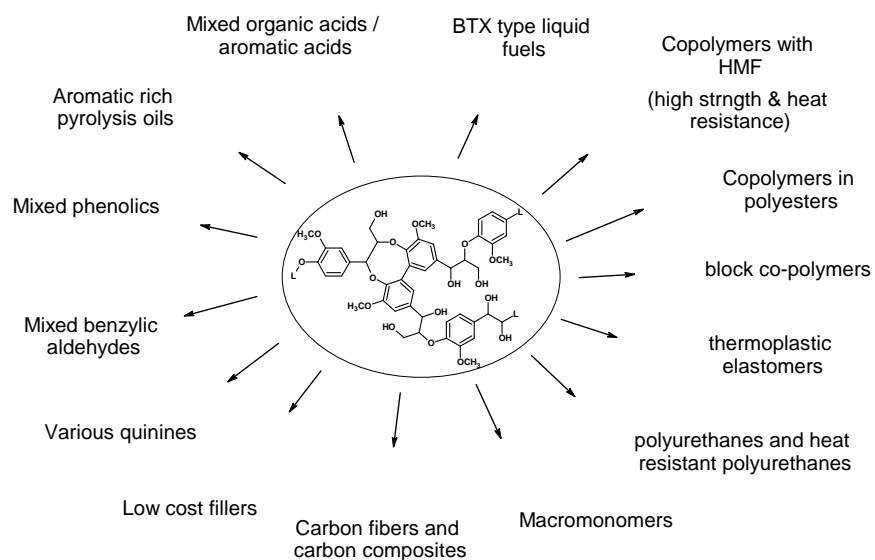
Figure A.10 – New Product Opportunities from Lignins

As described in Section 5 of the report, this initial evaluation provided a very large number of potential lignin products and a group of associated conversion technologies. These materials were downselected to the most promising group of candidates. These remaining candidates were evaluated for inclusion in the top opportunities list based on a number of criteria.

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Appendix 3 - An Overview of Lignin's Structure

Lignin is a natural amorphous polymer made up of substituted aromatic structures. At the highest level, two types of lignin are recognized: 1) *native* lignin, which is lignin as it is present in biomass, and 2) *technical* lignin, which is lignin isolated from biomass through various processes. Several lignin review articles detail various areas of lignin structure, both native and technical.[21] The following overview will illustrate how lignin's structure leads to processing challenges. These challenges differ significantly from those presented by more homogeneous feedstocks such as sugars.

Lignin is considered the essential natural glue that holds all plants together. More specifically, lignin is a natural amorphous polymer made up of randomly branched and crosslinked aromatic units. Through crosslinking with cellulose carbohydrates, lignin confers strength, rigidity and flexibility as well as aiding in water transport and imparting a measure of protection against attack by marauding insects and microorganisms. Many structures have been proposed for lignin as it is found in nature (so-called "native" lignin). Any of these structures are approximations at best since lignin's structure is not identical for all varieties of plants. In addition, methods used for lignin extraction and isolation frequently modify its native structure.[22] The composition, molecular weight and even the amount of lignin available also differ by plant source. Generally, the abundance of lignin in biomass decreases in order from softwoods > hardwoods > grasses (Table A.2).

Table A.2 – Percent Lignin in Various Biomass Sources

Source	% Lignin
Softwoods:	27 - 33
Hardwoods:	18 - 25
Grasses	17 – 24

Regardless of its complexity, lignin's unifying structural feature is a branched and crosslinked network of C9 phenylpropenyl units. Biosynthetically, these C9 units are provided by the enzymatic dehydrogenative polymerization of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Coniferyl and sinapyl

21 Glasser, W. G., Northey, R.A.; Schultz, T. P. eds. Lignin: Historical, Biological and Materials Perspectives, ACS Symposium Series 742, American Chemical Society, Washington, DC, 1999; Johnson, D. K. Lignin, a Source of BioEthanol Co-Products; Aden, A; Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover, Report June 2002. NREL/TP-510-32438; Glasser, W. G.; Sarkanen, S. eds. Lignin Properties and Materials; ACS Symposium Series 397, American Chemical Society, Washington, DC, 1988.

22 McCarthy, J. L. Islam, A. in Lignin: Historical, Biological and Materials Perspectives, Glasser, W. G., Northey, R.A.; Schultz, T. P. eds. ACS Symposium Series 742, American Chemical Society, Washington, DC, 1999, chapter 1.

alcohol are the starting points for the formation of the well-known guaiacyl and syringyl structures of lignin (Figure A.11).

phenol units

Coumaryl alcohol   Coumaric acid   Hydroxycinnamic acid

Guaiacol units

Coniferyl alcohol   Ferulic acid

Syringol units

Sinapyl alcohol
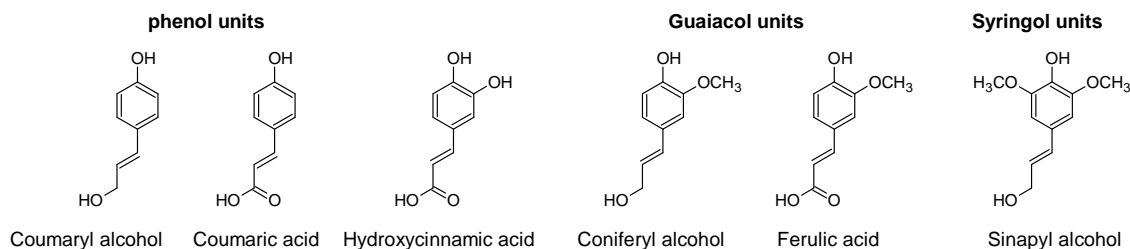
Figure A.11 - Types of C9 Units Found in Lignin

The relative proportion of these units depends on the lignin source (Table A.3). Softwoods are made up of guaiacyl units, whereas hardwoods contain both guaiacyl and syringyl units. Grasses additionally contain a variety of acidic guaiacyl units attached as esters and exhibit further substitution of *p*-coumaryl alcohols with *p*-coumaric, hydroxycinnamic, and ferulic acids. Softwood lignin is generally higher in molecular weight than hardwood lignin.

Table A.3 - Lignin Composition by Source

Source	Composition
Softwoods	Primarily derived from coniferyl alcohol (90%) with the remainder derived from *p*-coumaryl and sinapyl alcohols.
Hardwoods	Approximately equally derived from coniferyl and sinapyl alcohols.
Grasses	Primarily derived from coniferyl and sinapyl alcohols with 10 – 20% *p*-coumaryl alcohol.

Several common inter-unit linkages are found in native lignin upon biosynthetic polymerization of the various C9 units.[23] Some of the most important linkages found in lignin are shown in Figure A.12, along with their common designation. Table A.4 summarizes the relative proportion of some of these units as a function of source. The primary inter-unit linkage in native lignin is the β-O-4 linkage. This connectivity is thought to make up to 58% of the linkages present.

Trifunctionally linked units also provide numerous branching sites and ring units. Figure A.13 illustrates a hypothetical structure for a native softwood lignin based on estimates of the proportions of these substructural units.

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23 Sakakibari, A. Wood Sci. Technol. 1980, 14, 89.

It is important to recognize that native lignin undergoes profound structural changes and dramatic modification of molecular weight profiles depending on the isolation technology employed. Table A.5 exemplifies the physical property diversity for three technical lignin families.
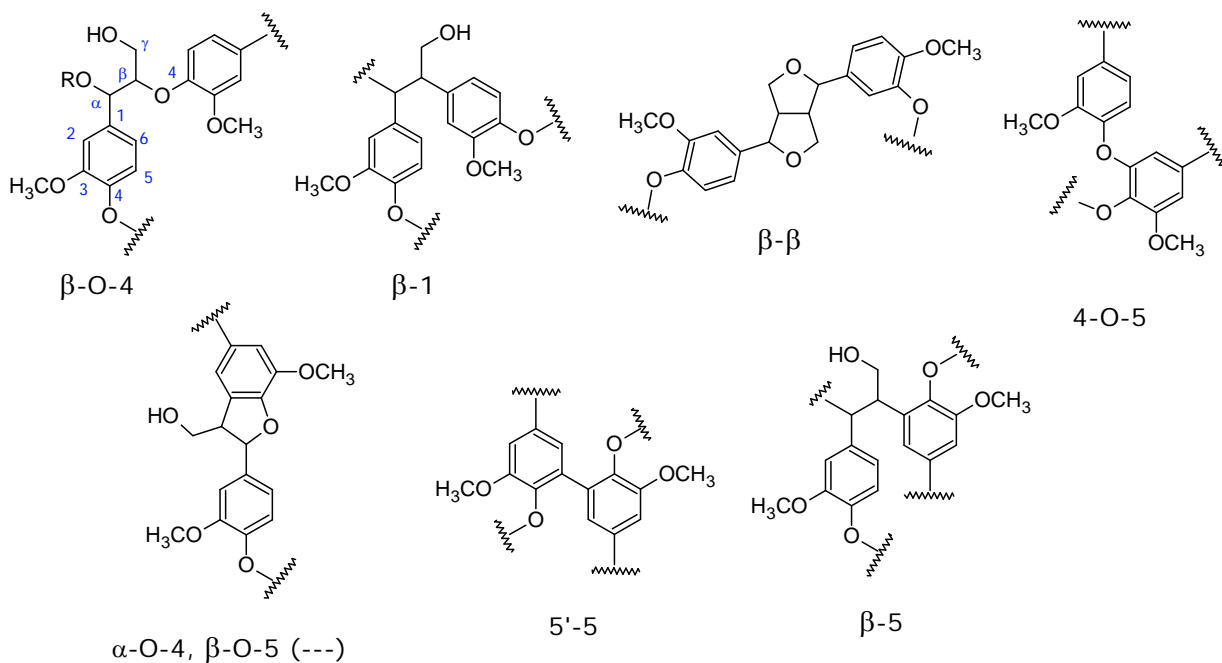
Figure A.12 - Primary Inter-unit Linkages in Native Lignin
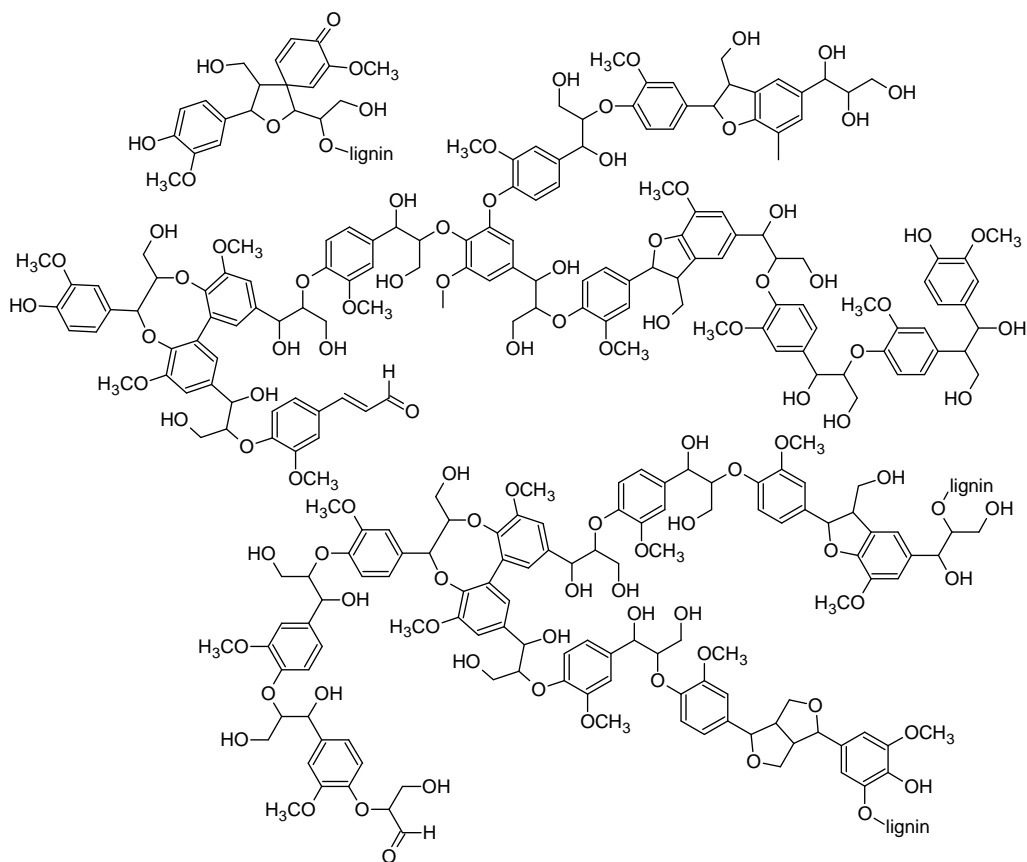
Figure A.13 - Structural motifs of softwood lignin (adapted from[23])

Table A.4 - Typical Distribution of Substructural Units in Lignin[24]

Lignin source	β-O-4	β-1	β–β	β-5	4-O-5	5-5
Poplar wood	57.8	2.1	2.1	1.8	0.7	0.7
Spruce wood	31.5	2.1	0.4	2.5	0.5	2.7
Pine kraft lignin	11.3	1.9	0.3	1.2	0.2	0.6
Birch kraft lignin	15.4	47.0	24.5	6.8	3.4	2.5
Aspen steam exploded lignin	25.9	17.0	37.8	12.6	4.5	2.2

24 Lapierre, C., Pollet, B., Monties, B. Proceedings, 8th International Symposium on Wood and Pulping Chemistry, Helsinki, Finland, 1995 (1) 131.

Table A.5 - Properties of Lignin by Extraction Technique[25]

Property	Lignosulfonates	Kraft lignins	Organosolv lignin
Molecular weight	20,000 - 50,000	2,000 - 3,000	< 1,000
Empirical formula*	$C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$	$C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$
Ave. monomer MW	215 – 254	180	188
Polydispersity	6 – 8	2 - 4	2.4 - 6.4
Sulfonate (meq/g)	1.25 - 2.5	0	0
Organic sulfur (%)	4 - 8	1 - 1.5	0
Color	Brown	Brown	Brown
Solubility	Soublel in H_2O (all pH's) Insoluble in organics	Soluble in alkali (pH >10.5), DMF, methyl cellosolve	Insoluble in water soluble in alkali and many organics

* Empirical formula estimated for softwood lignin

25 Lebo, S. E. Jr., Gargulak, J. D., McNally, T. J. Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition [Online]. John Wiley & Sons, Inc. 2001.

Appendix 4 - Potential Sources of Biorefinery Lignin

One of the biorefinery-level challenges for lignin is the choice of the lignin separation/isolation process to be employed. The following examples demonstrate the diversity of lignin sources that could reasonably be incorporated into the biorefinery along with their possible advantages and disadvantages. It is most likely that only a few will offer the kinds of flexibility necessary to serve as a feedstock. The following descriptions are not listed in an order of priority since each possesses a unique range of advantages and disadvantages. A biorefinery's choice will hinge on many factors including product output profile, accessibility to feedstock, business model, and type of feedstocks in the vicinity of the refinery.

Kraft Lignin

Kraft pulping is the dominant chemical pulping process in the world. The process is conducted at high pH in the presence of substantial amounts of aqueous sulfide, sulfhydryl and polysulfide and at temperatures in the range of 150-180 °C for around two hours. The chemistry of pulping reactions has been the subject of much study, and good summaries are available in the literature.[26]

The majority of the solubilized lignin is captured in the spent pulping liquor ("black liquor") along with most of the wood's hemicellulose. The lignin contained in black liquor serves as a fuel for much of the operation of a typical kraft mill. Black liquor is normally concentrated via multiple effect evaporators to 40-50% solids and then burned for its heating value (about 12,000 to 13,000 Btu/dry lb). The heat released is used for steam and power generation. Some of the heat released and part of the reducing value in black liquor is used to drive the mill's chemical recovery operation. This results in nearly all of the sulfur and caustic value being recycled to the process. Lignin is an important fuel for paper and pulp manufacturers as it contributes heavily to a pulp mill's energy self-sufficiency.

In a forest biorefinery, kraft lignin may be recovered from the black liquor by lowering the pH. Typically, this is done with carbon dioxide captured from the boiler's flue stack or with mineral acids. On lowering the pH, a substantial portion of the kraft lignin is precipitated and may be recovered by filtering and washing. Given the high-sulfur environment of kraft pulping, the sulfur content of precipitated and washed kraft lignin is surprisingly quite low, typically less than 1-2% which is consistent with the number of –SH linkages created during the kraft pulping process. Moreover, it can be almost free of sugars.

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26 Nimz, H. H. Ullmann's Encyclopedia of Industrial Technology, Wiley-VCH Verlag GmbH&Co. KGaA.

The availability of kraft lignin may be limited since MeadWestvaco is currently the only domestic producer at their Charleston, South Carolina operation. Approximately 70-75% of their isolated lignin is chemically sulfonated using one of two processes. In the first, kraft lignin is treated at about 100 °C with a mixture of chemicals typically used in sulfite pulping (aqueous sulfur dioxide, bisulfite and monosulfite at pH 2-12). This process introduces sulfonate functionality into the aliphatic side chains of lignin giving a material structurally related to sulfite lignin. At higher temperatures (150-200 °C), sulfonation will also occur on the aromatic rings. The sulfonated lignin is recovered by water removal or by precipitation with excess lime as calcium lignosulfonates. Sulfonylation at aliphatic, benzylic or aromatic sites confers solubility and surfactant qualities to the lignin. A second process uses acid induced hydroxymethylation of lignin's aromatic rings moieties with formaldehyde, again followed by treatment with sulfite pulping chemicals. Below 100 °C, sulfonate groups are formed at the hydroxymethyl site by nucleophilic substitution of OH with sulfonic acid groups. Above 100 °C, aromatic ring sulfonylation begins to occur.

The degree of sulfonation can be controlled so that products similar to or significantly different than sulfite mill-derived product can be manufactured. Since the lignin depolymerization and solubilization chemistries of kraft and sulfite pulping are somewhat different, the chemical properties and reactivity of sulfonated kraft lignin is slightly different than sulfite derived lignosulfonate. However, the physical, solubility and dispersant properties of the two types can be similar. Generally, the objective of sulfonylation of kraft lignin is to make a product that is essentially equivalent to sulfite mill-derived lignosulfonate and can effectively replace it in applications.

An estimated 25-30% of MeadWestvaco's total recovered kraft lignin is sold without further chemical modification. This unsulfonated kraft lignin is soluble in alkali at pH greater than about nine and reasonably soluble in strongly polar organic solvents. Its number average molecular weight (M_n) is generally between 1000 and 3000, but exhibits a polydispersity typically between 2 and 4 although it can be as high as to 8 or 9. Such values of polydispersity are typical of industrial grade polymeric materials. Polydispersity and functional group analysis suggests the average monomer molecular weight is around 180. A "molecular formula" of $C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$ has been reported for softwood kraft, and a model structure for kraft lignin has been reported (Figure A.14). Nearly 4% by weight is typically free phenolic hydroxyl.[27]

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27 Lebo, S.E. et al, Lignin, Kirk-Othmer Encyclopedia of Chemical Technology, p. 18 of on-line version, (2001), John Wiley & Sons, Inc.
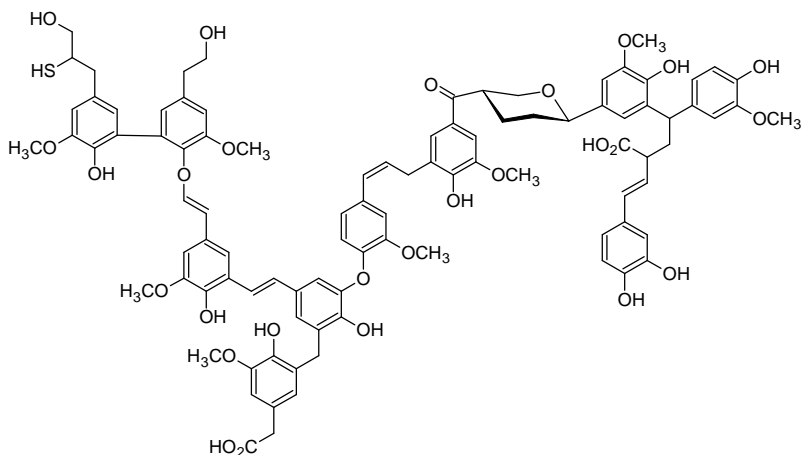
Figure A.14 - Model Structure for Kraft Pine Lignin (from ref [28])

Kraft pulping of wood is potentially the source of the largest amount of lignin for the biorefinery. Moreover, the pulp and paper industry has a highly efficient infrastructure for growth, harvesting, transport, and processing of forest materials. However, the kraft process is not likely to serve as a reasonable source of lignin raw material for biorefinery operations. Kraft operations are highly integrated and depend on the lignin fraction from wood as a fuel to operate the incredibly expensive chemical recovery boilers that are the heart of their operation. Diverting this fuel source to other uses would require the pulping operation to supplement its energy needs by purchasing natural gas or coal, potentially upsetting the mill's economics. Alternatively, energy losses could be mediated by using forest residues.

Nonetheless, opportunities exist for kraft lignin if the pulp and paper industry transitions to black liquor gasification. In that scenario, the industry could continue to generate the power they need, but because of the higher efficiency of gas turbines, could also produce a separate syngas stream for the production of higher-value products. Historically, evolution within the pulp and paper industry has been slow. Mill managers do not generally exercise options such as these. Thus, tapping into a kraft lignin stream to find a source of renewable carbon for the biorefinery could be difficult. Even MeadWestvaco is isolating only a small portion of the lignin available in their plant. Their lignin facility is part of a 692×10^3 tonne/yr pulping operation and produces about 20×10^4 tonnes/yr of lignosulfonate, which is only about 5.8% of the total lignin available in the mill.[29]

28 Gargulak, J. D., Lebo, S. E. in Lignin: Historical, Biological and Material Perspectives; Glasser, W. G., Northey, R. A., Schultz, T. P., Eds., ACS Symposium Series 740; American Chemical Society: Washington, DC, 1999; pp. 304-320.

29 Calculated as follows:

       692x103 tonnes/yr pulp = approx. 1384x103 tonnes/yr wood feedstock

       1384x103 wood feedstock = 346x103 tonnes lignin/yr (assuming 25% lignin in feedstock)

       20x103 tonnes lignosulfonate/346x103 tonnes lignin/yr = 5.5% of lignin converted to lignosulfonate

       Source: Chemical Economics Handbook "Lignosulfonates".

Sulfite Lignin (Lignosulfonates)

The sulfite pulping process is a potential source of forest biorefinery lignin because in contrast to kraft pulping, sulfite pulping generally does not recover pulping chemicals making a lignin-rich black liquor stream available for conversion to chemicals. Because of the nature of the sulfite process, the isolated lignin contains considerable sulfur in the form of sulfonate groups present in the aliphatic side chains. In North America, Lignotech produces about 120 x 10^3 tonnes/yr of lignosulfonate by purchasing sulfite liquors from nearby mills.[30] Worldwide, about 1060 x 10^3 tonnes of lignosulfonates are produced annually, again primarily from sulfite black liquor. The chemistry of sulfite pulping has been a subject of much study, and good summaries can be found in the literature.[31] Commercial sulfite pulping pre-dates the kraft process but has largely been replaced by kraft pulping due to the stronger fiber produced by the latter.

Sulfite pulping is carried out between pH 2-12, depending on the cationic composition of the pulping liquor. Most sulfite processes are acidic and use calcium and/or magnesium as the counterion. Higher pH sulfite pulping is generally done with sodium or ammonium counterions. Sulfite lignin generally is soluble throughout the entire pH range so it cannot be readily isolated by simple pH adjustment. Thus, recovery of sulfite lignin (lignosulfonate) is commonly done from waste pulping liquor concentrate after stripping and recovery of the sulfur. Precipitation of calcium lignosulfonate with excess lime (Howard process) is the simplest recovery method, and up to 95% of the liquor's lignin may be recovered. It appears to be preferred especially when calcium lignosulfonate product is desired. Other recoveries are known, but none appear to be practiced commercially due to cost factors. Historically, sulfite pulping has been used as a source of fermentable sugars from low-pH sulfite liquor. Tembec has operated a sulfite mill in Canada in this fashion and uses these sugars for ethanol production.

Sulfite lignin has a higher average molecular weight than kraft lignin. M_w values of 1,000 and even up to 140,000 have been claimed although values of 5,000-20,000 are more common.[32] Their polydispersity is higher than kraft (4 to 9), and they have higher sulfur content (3% to 8%). Sulfite monomer molecular weights of 215-254 have been calculated. Lignosulfonates are generally soluble in water throughout almost the entire pH range. They are also soluble in some highly polar organics and amines.

Approximate "molecular formulas" of $C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$ for softwood sulfite lignin and $C_9H_{7.5}O_{2.5}(OCH_3)_{1.39}(SO_3H)_{0.6}$ for hardwood sulfite lignin have been claimed, and a model lignosulfonate structure has been reported (Figure A.15).

30Chemical Economics Handbook, Lignosulfonates

31 Lin, S. Y., Lin, I. S. in Ullmann's Encyclopedia Industrial Chemistry, 5th ed., Vol. 15, VCH, Weinheim, Germany, 1990, P. 305.

32 Yean, W. Q., Goring, D. A. I. Svensk Papperstidn. 1952, 55, 563; Sjostrom, E. et. al., Svensk Papperstidn. 1962, 65, 855; Brogdon, B.N., Dimmel, D.R. J. Wood Chem. Technol. 1996,16, 297.
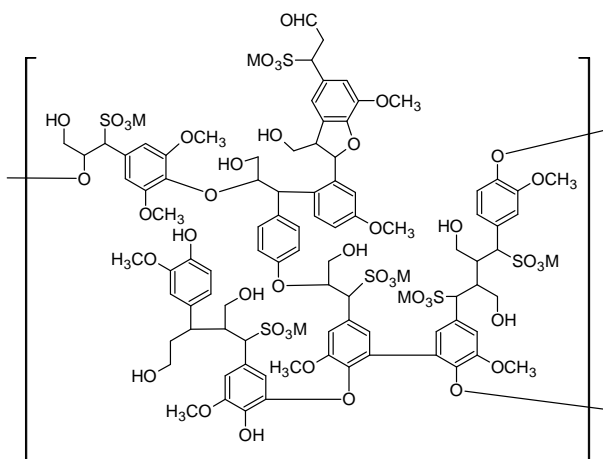
Figure A.15 - Model Structure for Lignosulfonate (from[19])

Sulfite lignin is hampered by several disadvantages. The first is availability. Sulfite pulping accounts for only about 2% of the total pulp production in the United States and only produces about 1.1×10^9 lb/yr of lignin. Assuming that this lignin would be available for a compound with molecular weight 150, only about a billion lb/yr could be produced.[33]

In addition, lignosulfonates are generally impure materials and contaminated by the cations used during pulp production and recovery. Lignosulfonates are normally mixtures, only 70-75% of which is actually lignin. The remainder is primarily carbohydrate, ash, and other inorganic materials. Commercial lignosulfonates also show wide molecular weight profiles and variable degrees of sulfonation.[34] Fractionation of commercial samples can be carried out to give lower molecular weight materials but the polydispersity of commercial feedstocks could lead to a large number of fractions.[35] Incorporation of the sulfur into final biorefinery products could be a serious problem, and its removal would add expense and/or environmental difficulties.

Organosolv Lignin

Solvent processes offer a good opportunity for supplying lignin to the biorefinery. Organosolv pulping is a general term for the separation of wood components through treatment with organic solvents. Such operations normally give separate process streams of cellulose, hemicellulose and lignin. For example, a well recognized laboratory method for extracting lignin from

33 Smith, B. R., Rice, R. W., Ince, P. J., Pulp Capacity in the United States, 2000, USDA Forest Service, General Technical Report FPL-GTR-139; Pulp and Paper North American Factbook 2001, Paperloop Publications (2002).

34 Fredheim, G., Braaten, S. M., Christensen, B. E., J. Chromatog. 2002, 942, 191; Buchholz, R. F., Neal, J. A., McCarthy, J. L. J. Wood Chem. Tech. 1992, 12, 447.

35 Freheim, G. E., Braaten, S. M., Christensen, B. E. J. Wood Chem. Tech. 2003, 23, 197.

wood involves heating it in aqueous dioxane at elevated temperatures. Such an approach affords a lignin that retains much of its original structure in the form of β-O-4 inter-unit linkages. A wide variety of solvents and combinations have been proposed for organosolv pulping. Many include acids or alkali to enhance pulping rates. The most well known is the Allcel process,[36] which uses ethanol or ethanol-water as solvent. This was demonstrated at a pilot scale by Repap Enterprises in Canada in 1989 but is no longer operational.

Organosolv processes offer several possible advantages as a source of biorefinery lignin. In general, the processes result in separate and easily isolated streams of cellulose, hemicellulose, and lignin. Specifically, organosolv lignin can be easily separated from the pulping solvents either by solvent removal and recovery or a combination of precipitation with water accompanied by distillation to recover solvent. Organosolv processes are also considered more environmentally friendly than sulfite or kraft pulping.

Most organosolv lignin is insoluble in water between pH 2 and 7 but will dissolve in alkali and many polar organic solvents. M_n values are typically less than 1000, and polydispersity may range from about 2.4 to 6.4. An approximate molecular formula of $C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$ and a calculated molecular weight of 188 have been reported. Organosolv lignin tends to be more like unsulfonated kraft lignin than sulfite-derived lignosulfonate. The lower molecular weight and low sulfur content may make organosolv lignin attractive as a source of low-molecular weight phenols or aromatics.

The NREL Clean Fractionation (CF) process gives an example of the use of organosolv technology in a biorefinery context. This process was developed primarily as a method to separate wood into its three major components (Figure A.16).[37]
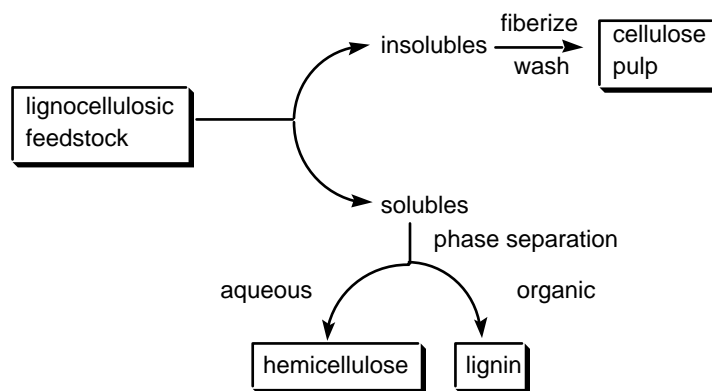

Figure A.16 - The NREL Clean Fractionation Process

36 McDonough, T. J. Tappi J. 1993, 76(8), 186; Schroeter, M. C. Tappi J., 1991, 74 (10), 197; Varshney, A.K.; Patel, D. J. Sci. Ind. Res., 1988, 47(6), 315; Aziz, S.; Sarkanen, K. Tappi J., 1989, 72(3), 169.

37 Black, S. K.; Hames, B. R.; Myers, M. D. U S patent 5,730,837 to Midwest Research Institute (1998).

The process treats the biomass with a ternary mixture of methyl isobutyl ketone (MIBK), ethanol, and water in the presence of an acid promoter. The great majority of the work has been carried out using a 16/34/50 ratio of MIBK/EtOH/H$_2$O for 56 minutes at 140 °C in the presence of 0.05 – 0.2M H$_2$SO$_4$ as standard conditions. The solvent mixture selectively dissolves the lignin and hemicellulose components leaving the cellulose as an undissolved material that can be washed, fiberized, and further purified. The soluble fraction containing the lignin and hemicellulose is treated with water causing a phase separation to give an organic phase containing the lignin and an aqueous phase containing the hemicellulose. CF appears to be a very general process and can be used for fractionation of a wide range of biomass feedstocks including corn stover, newsprint, bagasse, corn fiber and rice straw. Dried CF lignin is isolated in high yield as a shiny, brown, free-flowing powder. It exhibits properties consistent with other organosolv lignins including a generally lower molecular weight profile and a greater solubility in polar organic solvents.

Organosolv processes possess some disadvantages. They incur higher costs associated with the handling and recovery of the organic solvent. Organosolv lignin also tends to be much less water soluble, which may limit its use in some applications. Currently, there is no commercial source of organosolv lignin. Recently, however, the Lignol Innovations Corporation of Vancouver B.C., Canada acquired all of Alcell's technology and IP portfolio and is poised to once again begin Alcell-type organosolv pulping on a commercial scale. [38] The flexibility and generality of organosolv processes, combined with easy access to a lignin stream, suggests that it should be ranked higher than kraft or sulfite processes.

Pyrolysis (Pyrolytic) Lignin

Pyrolytic processes (thermal decompositions occurring in the absence of oxygen) can be used to produce a lignin stream for potential biorefinery use. Virtually any form of biomass can be considered for fast pyrolysis. While most work has been carried out on wood due to its consistency and comparability between tests, nearly 100 different biomass types have been tested by many laboratories over a wide range of agricultural and forestry wastes.

Using carefully controlled fast pyrolysis conditions (reaction temperature of around 500 °C, vapor phase temperature of 400 - 450°C, and short vapor residence times of typically less than 2 seconds), it is possible to generate a bio-oil, generally from whole biomass, in yields of up to 75 weight % on a dry feed basis.[39] The byproducts from biomass pyrolysis are char and gas,

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38 The Lignol Innovations Corp. of Vancouver BC, Canada, has acquired all of Allcel's technology and IP portfolio and is poised to once again begin Allcel type Orgnosolv pulping on a commercial scale. See www.lignol.ca and www.lignol-innovations.com.

39 http://www.pyne.co.uk/

which are used within the process to provide the process heat requirements. There are no waste streams other than flue gas and ash.

It is possible to isolate a dry powder that has been termed "pyrolytic lignin" by adding pyrolysis oil to ice-cooled water while stirring. After washing and drying under vacuum, a light to dark brown powder is obtained that is derived mostly from the lignin originally present in the pyrolyzed biomass. Scholze et al. published extensive characterization data on the composition of pyrolytic lignins obtained from hardwoods, softwoods and wheat straw obtained from a number of different pyrolysis units. The largest difference between pyrolytic lignins and the lignin in biomass is the very low molecular weights of pyrolytic lignin indicating the high degree of depolymerization caused by the thermal treatment of pyrolysis and suggesting that pyrolysis may be useful as a technology for the controlled molecular weight reduction of lignin. Scholze et al. reported M_w values of 600-1300 and M_n values of 300-600 for pyrolytic lignins, indicating the presence of dimeric to nonameric phenolic units.[40] ^{13}C-NMR spectra of the pyrolytic lignins confirmed the fundamental changes in the lignin structure that occur during pyrolysis. Evidence was seen for drastic depolymerization and also formation of new carbon-carbon bonds, particularly at the C5 position in hardwood-derived lignins (where methoxyl groups are normally found in syringyl units) and for the disappearance of aryl-alkyl ethers. Schulze et al. proposed a C8 repeat unit for pyrolytic lignin rather than the C9 unit normally used. The empirical formula was $C_8H_{6.3-7.3}O_{0.6-1.4}(OH)_{1-1.2}(OMe)_{0.3-0.8}$. These features suggest that pyrolytic lignin may offer some unique possibilities for conversion to useful aromatics when compared to other biorefinery lignin sources. The disadvantage to pyrolysis lignin is the high level of carbohydrate consumption that occurs if a lignocellulosic feedstock is used. Use of pyrolysis requires process technology that retains a carbohydrate component for use in the sugar platform.

Steam Explosion Lignin

The steam explosion process is a rapid and decades old treatment process for lignocellulose that releases individual biomass components through steam impregnation under pressure followed by rapid pressure release.[41] The treatment of wood or bagasse is carried out using high-pressure steam (200-500 psig, 180-230 °C) at short contact times (1-20 minutes). Both continuous and batch variants are known, and the process has generally been used as a method for preparing cellulose pulp. However, steam explosion also serves as an excellent source of lignin. When hardwoods are employed, more than 90% of the lignin in the wood can be obtained from the explosion product by subsequent washing with alkali or by extraction with organic solvent. Softwoods are more recalcitrant but can also serve as a

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40 Scholtze, B., Meier, D., J. Anal. Appl. Pyrolysis 2001, 60, 41; Scholtze, B., Hanser, C., Meier, D., J. Anal. Appl. Pyrolysis 2001, 58-59, 387.

41 Avellar, B. K., Glasser, W. G. Biomass Bioenerg., 1998, 14, 205.

lignin source by treating the exploded pulp with alkaline peroxide.[42] The process itself appears to retain much of the original lignin structure but some changes may occur upon isolation.[43] Steam explosion lignin appears to be similar to organosolv lignin in overall properties, exhibiting both a lower molecular weight and higher solubility in organics than kraft lignin.[44] Its structure is believed to consist of phenolic oligomers with between 3 and 12 benzene rings per oligomer unit.[29] Thus, steam explosion lignin may be an interesting candidate for selective conversion of lignin to a relatively narrow fraction of mixed phenols.

An obvious advantage of the steam explosion process is freedom from the sulfur-related environmental concerns of the kraft and sulfite processes. Similar to organosolv processes, it is capable of co-producing a sugar stream for fermentation and/or conversion to chemicals along with the lignin. Thus, it may become a potentially attractive process for a biorefinery centered on fuel ethanol, chemicals, lignin derivatives and cellulose pulp. A disadvantage of steam explosion pulping is that it is not practiced commercially in the United States, presumably due to a combination of non-competitive economics, low pulp yields and only moderate quality pulp. Solving these problems could make this process viable in the longer-term. StakeTech Technology of Norval, Ontario, Canada continues to offer a commercial process and proprietary machinery to conduct steam explosion pulping.[45] Steam explosion possesses many of the same advantages as organosolv processes.

Dilute acid lignins

A wide range of biomass fractionation technologies based on the use of aqueous acid has been investigated. The primary focus of these processes is the isolation and hydrolysis of the cellulose portion of biomass as an EtOH feedstock. However, each will also provide a lignin-containing stream as a byproduct.[46] Treatments with both concentrated and dilute acids are well known as methods for the hydrolysis of cellulose. Commercial processes for acid hydrolysis were known in the early part of the 20th century and have the advantage of being chemically inexpensive and straightforward. However, several disadvantages of these processes have been reported. Very effective separation can be realized at high acid concentrations. However, corrosion-resistant reactors and an effective acid recovery process are needed for the separation, which raises the overall cost.

42 Shevchenko, S. M., Beatson, R. P., Saddler, J. N. Appl. Biochem. Biotech. 1999, 77-79, 867.

43 Hua, X., Capretti, G., Forcher, B., Marzetti, A., Kokta, B. V., Kaliaguine, S. Appl. Spectroscopy, 1993, 47, 1693.

44 Wayman, M., Lora, J. H. Tappi J., 1978, 61(6), 5526. U. S. Patent 4,136,207; U. S. patent 4,186,658; Shimizu, K. et al., Biomass Bioenergy, 1998, 14(3), 195.

45 Heytz, M. et al, Bioresource Technol., 1991, 35, 23.

46 Sun, Y., Cheng, J. Biores. Tech. 2002, 83, 1.

NREL has developed single-stage dilute acid hydrolysis as a method to fractionate biomass under mild conditions. Considerable work has been carried out to optimize and evaluate this process. Since it is a leading candidate for use as a biorefinery "front end," its utility as a source of lignin feedstock should be considered. Although dilute acid treatments minimize the problems seen at high-acid concentrations, a number of kinetic models indicate that the maximum conversion of cellulose to glucose under these conditions is 65 – 70%. This limitation occurs because subsequent degradation reactions of the glucose to 5-hydroxymethylfurfural and levulinic acid take place.[47] Depending on how the process is carried out, several different types of lignin residues exhibiting a wide range of properties can be isolated. A potential disadvantage to this lignin source is that the yield is low, recovering only about 50% - 70% of the available lignin. The lignin also generally contains sugar-derived contaminants. It is possible to further upgrade this lignin fraction using specialized conditions. However, this approach generates very dilute process streams, requires specific materials of construction, and is difficult to scale up economically.

Dilute acid lignin should be seriously considered as a feedstock for chemical production but the practice of this technology highlights an important feature for lignin use. Currently, dilute acid lignin exhibits sufficient properties for fuel use. However, lignin must be removed earlier in the process and under milder conditions if it is to be used as a feedstock for chemical production. It is anticipated that the conversion of this lignin into higher-value products will offset any increased cost in more sophisticated lignin removal.

Lignin removal from biomass, wood in particular, can also be done via electrophilic substitution reactions on the aromatic portion of the structure. Both nitric acid and N_2O_5 have been investigated for this. The pulp is similar in properties to acid sulfite pulp. Similarly, acidic chlorine dioxide has been proposed and in fact piloted in the United States and Japan as the holopulping process. Nitric acid lignins are not recovered from the spent pulping liquor since most of the liquor is used after some concentration as a nitrate fertilizer. Because of high costs and environmental concerns neither nitric nor chlorine dioxide pulping have any commercial use in the United States.

Alkaline Oxidative Lignin

Pulping can also be done via alkaline oxidation using, for example, O_2 or H_2O_2. These processes degrade and solubilize lignin via chemistries somewhat different than kraft or sulfite pulping. Alkaline lignin may be easily recovered by lowering the pH or by concentration and filtering and drying. Its solubility properties are different enough from conventional lignosulfonates that it is not easily accommodated in current commercial applications.

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47 Torget, R. W., Kim, J. S., Lee, Y. Y. Ind. Eng. Chem. Res. 2000, 39, 2817.

Unfortunately, delignification rates for alkaline oxidative pulping tend to be slower and the pulp weaker than kraft pulp. Thus, alkaline oxidation is not widely practiced and the respective lignin is not readily available. Alkaline oxidative lignin tends to be low in molecular weight and also features more carbonyl and carboxyl functionalities than kraft or sulfite lignin.

Other Lignin Processes

There are many reports of other processes that include various chemical and mechanical steps for recovering lignin. Hot water can be used as a fractionating medium for biomass. The resulting lignin would be expected to be similar to solvent or dilute acid lignin. The ammonia fiber explosion (AFEX) process[48] has been examined for biomass separation but as yet does not offer a well-defined lignin stream.

An overview of what process might be compatible with what lignin sources is provided in Table A.6.

Table A 6 – Biomass Separation Processes Available to the Biorefinery

Isolation Technique	Softwood	Hardwood	Ag. Residue
Kraft	X	X	
Sulfite	X		?
Solvent		X	X
Pyrolysis	X	X	X
Steam Explosion		X	X
Dilute Acid		X	X
Hot Water		X	X
AFEX			X
Alkaline/H_2O_2			X
Other acid lignins		X	X
Alkaline	X	X	??

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48 Kim, T. H., Kim, J. S., Sunwoo, C., Lee, Y. Y. Bioresource Technol. 2003, 90, 39.

Appendix 5 - Emerging Lignin Opportunities

Lignin Pyrolysis

Lignin may be pyrolyzed to yield a liquid product and an ash. The current state of the art in pyrolysis processing of biomass is called fast pyrolysis or flash pyrolysis. It is accomplished in a number of reactor types, most commonly in fluidized beds or circulating fluidized beds. Typical processing conditions are 0.5 seconds at 500 °C at 1 atm with an inert atmosphere and inert solid particle heat carrier. Dry feedstock is a prerequisite for this process; therefore, wet lignin from most pulping processes or as a byproduct from an aqueous-based biorefinery is incompatible with pyrolysis and must be dried before entering a pyrolysis process.

Through fast pyrolysis, wood can be liquefied to form pyrolysis oils containing biopolymer components in water and light oxygenates such as acetic acid, hydroxyacetaldehyde and hydroxyacetone among many others including guaiacol and alkylated guaiacols.

Fast pyrolysis is still in its commercial infancy having been under development only since the early 1980s. To date, the only commercial application is the production of food flavoring chemicals from hardwood via extraction of smoke-flavor components from the pyrolysis oil aqueous phase. Extensive research has been carried out within the U.S. Department of Energy program on ways to recover lignin-derived phenolic components from this oil for use in resin manufacture. However, these technologies are still not economically attractive. Work at the National Renewable Energy Laboratory (NREL) has focused on a solvent-recovered phenolic stream to displace phenol in phenol-formaldehyde resins. More recently, Ensyn has attempted to make a resin additive by distilling the light oxygenate components from the residue remaining after recovering flavor chemicals.

The major barrier to the use of pyrolysis oil for chemical production is its complex nature. Whole wood as feed makes a more complex oil product than would be expected from relatively pure lignin. The thermal processes involved in the formation of the oil result in a very diverse collection of biopolymer fragments. The lignin-derived portion of the oil maintains much of the structural information of the original biomass as evidenced by the ability to determine the source biomass leading to those components. Although the phenolic structural unit is commonly present, it exhibits several different substitution patterns. In order to use these sorts of products, a market must identify uses for mixtures of similar, and substituted, compounds instead of the conventional demand for pure single components.

Separation of the lignin-derived components from oil has been reported; but results from Pacific Northwest National Laboratory (PNNL) suggest that the

report is over-simplified. The process is water-based, wherein the lignin-derived components are precipitated and recovered from the oil by water addition. PNNL analysis suggests that the resulting water and solid organic phases are far from pure with considerable cross-contamination of the individual phases. However, washing can isolate high-molecular weight lignin oligomers. Using relatively pure lignin instead of whole wood for the pyrolysis feedstock would likely eliminate much of this difficulty.

Further development of pyrolysis oil processes can also be expected to yield useful chemical components. Previous work has focused on liquid fuels production by both hydrogenation and catalytic cracking. In the hydrogenation case, hydrocracking and hydrodeoxygenation were conducted in an effort to produce an aromatic gasoline. The lighter cellulosic-derived components generated a light gas byproduct that was reformed to produce hydrogen feed. More recent hydrogenation studies (at PNNL) have focused on hydrogenation to produce other chemical products such as cyclohexanols. One significant problem for hydrogenation is that the high water content of bio-oil leads to chemical and physical degradation of the typical alumina catalyst supports. This issue would need to be addressed to practice hydrotreating effectively.

In the catalytic cracking case (absence of added hydrogen), the phenolics led to high levels of coke formation on the catalyst that required combustion for regeneration. This phenomenon is, of course, also observed in conventional petroleum catalyst crackers. In the case of pyrolysis oil, many of the oil components are too large to react effectively in the active catalyst pores. Thus, the yields of useful cracked products were relatively low.

Lignin pyrolysis still needs further development to determine if it can be economically viable. The establishment of a bio-oil production industry is necessary to provide a source of bio-oil for further development of the lignin-derived products. A key element of economic success depends on finding a cheap source of a desirable lignin feedstock.

Anthraquinones

Certain anthraquinone (AQ) derivatives can be used in existing kraft processes to increase pulping rates and product yields and have been the focus of an industry-wide evolution of pulping from high to low to sulfur-free methodology. Pulping catalyzed by AQ holds the promise of addressing problems with plant bleach effluents by producing pulps that are more easily bleached than standard kraft pulps. Modifying the cooking process reduces the amount of residual lignin present in the pulp before bleaching. Joint work between NREL and the Institute of Paper Science and Technology led to an inexpensive synthesis of mixed quinones from lignin and development of

several systems for selective lignin oxidation including Co-superoxo complexes, heteropolyacids, and NO_2/O_2.[49]

The approach uses a low-molecular weight (LMW) lignin fraction from a whole lignin-containing source. The LMW lignin is converted to AQ, or AQ-like products in two chemical steps. First, oxidation of the LMW lignin gives a mixture of two key intermediates, monomethoxybenzoquinone (**1**) and dimethoxybenzoquinone (**2**). In the second step, isoprene is added to **1** and **2** to give a mixture of 2,6- and 2,7-dimethylanthraquinone (**3**, DMAQ) and other quinone products. While other dienes, such as butadiene, can be used in the second step, DMAQ is a more active pulping catalyst than nonmethylated AQ, or more fully methylated AQ (Figure A.17).
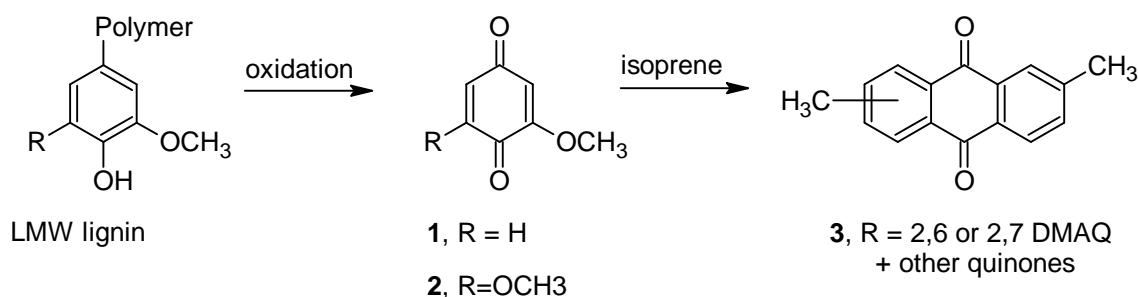
Figure A.17 - Preparation of Quinones from Lignin

As anticipated, the reaction between lignin-derived **1** and **2** and a diene led to a mixture of products. Interestingly, this mixture exhibited catalytic activity in pulping tests equal to or greater than AQ itself. However, the appearance of cheap imported AQ from China made application of this technology in the pulp and paper industry less important. Still, the ability to selectively oxidize lignin to quinones suggests that development of next-generation oxidation catalysts for lignin could offer an important opportunity for the biorefinery.

Emerging Fuel Markets

Since 1989, the U.S. Environmental Protection Agency has implemented regulations lowering the allowable Reid Vapor Pressure (RVP) of gasoline. Lowered RVP is achieved by reducing the amount of n-butane blended into the fuel and compensating with oxygenates. Similarly, gasoline with a minimum oxygen content of 2.7 weight percent must be sold during the winter months in carbon monoxide non-attainment regions. In 1993, 36 metropolitan areas fell into this category. In 1995, the Reformulated Gasoline

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49 Dimmel, D. R., Bozell, J. J., von Oepen, D. G., Savidakis M. C. in Advances in Chemical Modification, Properties and Usage of Lignin, Kluwer Academic, New York (2002), 199; Bozell, J. J., Hoberg, J. O., Dimmel, D. R., J. Wood Chem. Tech., 2000, 20, 19; Bozell, J. J., Hoberg, J. O., Dimmel, D. R. Tetrahedron Letters, 1998, 39, 2261; Bozell, J. J., Hames, B. R., Dimmel, D. R. J. Org. Chem., 1995, 60, 2398.

Program began in areas with severe year-round ozone pollution. The regulations limited the amount of benzene and other aromatics that could be present in gasoline and also required the addition of a minimum amount of fuel oxygenates.

The oxygenate market was dominated by methyl tertiary-butyl ether (MTBE) until tests in California showed that it leached into groundwater supplies. This generated bans on its use, which has led to increased emphasis on ethanol. Ethanol has a significant market share, particularly in Midwest regions where alcohol fermentation facilities are abundant. Methyl tertiary-amyl ether (TAME) is another oxygenate that has been gaining ground recently. Regulatory activity in California (year-round oxygenate levels on the order of 2%) may prove to be a driver for nationally mandated increases in oxygenate requirements. Thus, oxygenate market growth is anticipated to be greater than gasoline market growth.

Methanol-soluble nitrated lignin has shown ignition accelerating properties for methanol-fueled diesel engines. The potential of this application depends on methanol replacement of diesel, which is not economically viable without significant environmental drivers. For economic comparison, the lignin-based ignition accelerator can be compared with conventional technologies such as the addition of glow plugs or spark plugs. Chem Systems, Inc. estimates that there is a $0.46/lb opportunity for a lignin-based cetane enhancer to be competitive with the conventional plug technologies.

Polymer Applications

Applications are extensive, but until now have been used in very limited volumes, with many examples being academic in nature. Reported applications include:

- Precursors for low-cost carbon fiber (emerging, not yet well developed)
- Component of and catalyst for inherently conducting polymers
- Macromonomers in polyester, urethane and epoxy polymers
- Components in polymer blends and alloys
- Precursors to new generations of polyols
- Replacement for phenol-formaldehyde and urea-formaldehyde foams
- Sealants and adhesive resins

In these applications, positive features of low-cost, improved Tg (heat resistance), water resistance, and biodegradability are claimed but little emphasis is placed on the negative of lignin's color properties. Apparently, the end uses are in engineering or with polymers where color is not important.[50]

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50 Hu, T. H., ed., Chemical Modification and Usage of Lignin, Kluwer Academic Press, New York (2002), chapters 1-6.

Some paper industry experts believe that lignin could be more widely used as a polymer additive and blending agent. However, lignin's inability to be well dispersed in and strongly associated with the "backbone" structure of the polymers or plastics with which it may be blended will need to be overcome. Unmodified kraft lignin and lignosulfonate would rather associate with itself. This mutual incompatibility and mutual insolubility causes "islands" of lignin to form within a polymer blend that in turn result in weakness or brittleness instead of a reinforcing or strengthening effect. This issue is likely associated with lignin's polyelectrolyte character. Thus, organosolv, and acetylated or etherified lignins often perform better as polymer additives than do lignosulfonates.[51]

Other Lignin Uses in the Patent Literature

As part of this evaluation, a Chemical Abstracts patent search on the term "lignin" between 1980 and 2002 was carried out. The original search turned up about 2800 patents abstracts, which were read, scrubbed to remove non-relevant patents, and then sorted into categories. Most patents areas of known lignin use: agrochemical applications, batteries, cement, etc.

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51 Feldman, D. in Chemical Modification and Usage of Lignin, Kluwer Academic Press, New York, Hu, T. H. ed., Kluwer Academic Press, New York (2002), p. 81.

Appendix 6 – Known Lignin Uses and Suppliers

Lignin is a product of commerce, and a number of uses currently exist in industry. This appendix provides a brief summary of past and current commercial uses of lignin and a more extensive description of emerging lignin uses.

Power

The major use of lignin today is for fuel value and power generation in kraft pulping. Kraft lignin has about two-thirds of the fuel value of heating oil (17,000 Btu/lb. Black liquor gasification technology, if widely adopted by industry, could offer new opportunities for kraft lignin as a source of power. Considering the economic health of U.S. pulp mills, it is unclear whether the pulp and paper industry would also add the new capital infrastructure necessary for lignin recovery and conversion to chemical intermediates and products.

Current Commercial Lignin-Based Products

Almost all lignin in current commercial use is as lignosulfonates produced from spent sulfite pulping liquors. Westvaco and LignoTech Sweden also produce lignosulfonates by sulfonation of kraft lignin, but this process produces a product with a much lower molecular weight. Total lignosulfonate sales in 1996 were about $600 million at a capacity of 975 million tons.[18] Worldwide, production is dominated by Borregaard-LignoTech (Norway) and Tembec (Canada). MeadWestvaco, LignoTech and Georgia Pacific are the major U.S. producers, with MeadWestvaco being the sole commercial producer of unsulfonated kraft lignin globally. Lignin uses have been generally limited to applications in which the bulk properties such as solubility, surface activity and solids content are acceptable or important. A summary of commercial applications for lignin is shown in Table A.6 In addition, Figure A.18 and Tables A.7 – A.9 summarize currently available production data for lignosulfonates.
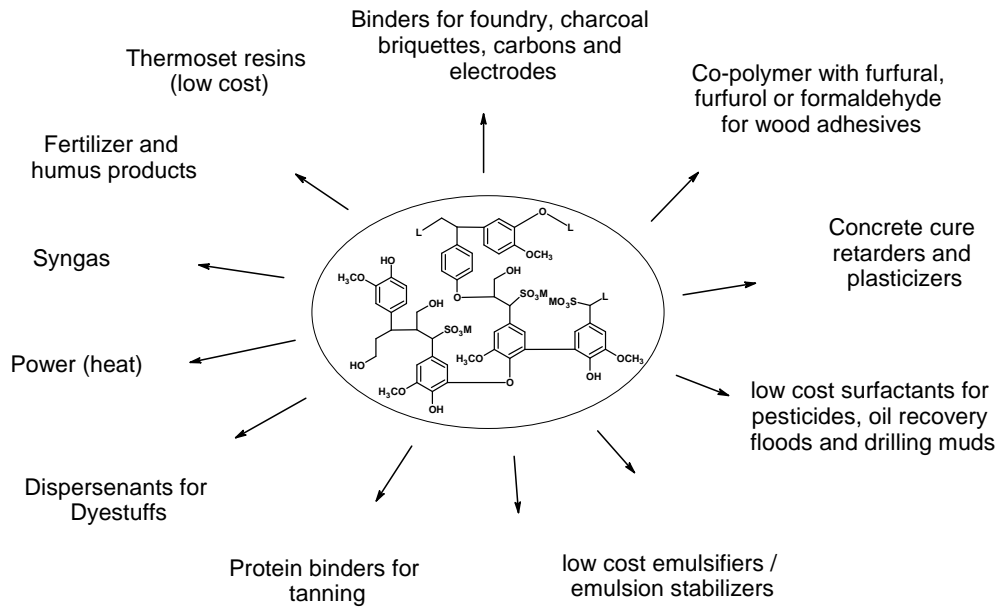
Figure A.18 - Current Uses and Products from Lignosulfonates

Table A.7 - Consumption of Lignosulfonates, 2001

Application	World Consumption (2001) - %
Concrete Admixture	45
Animal Feed Pellets	13
Road Binders, Dust Control	11
Animal Feed Molasses Additive	3
Pesticide Dispersant	5
Oil Well Drilling Muds	4
Dye Dispersant	12
Other	7

(Source: Chemical Economics Handbook)

Table A.8 - Lignosulfonate Consumption* and Average Growth Rate

	2001	2006	Ave Yearly Growth Rate
United States	291	284	-0.5
Canada	58	64	2.0
Japan	90	87	-0.7
W. Europe	318	338	1.2
Rest of World	297-315	262-287	-2.5
Total	**1,053-1,074**	**1,035-1,060**	**-0.3**

*1000s to MT, solids basis (Source: Chemical Economics Handbook)

Table A.9 - Lignosulfonate Consumption by End Use and Region

	Use by Percent					Totals	
	United States	Canada	W. Europe	Japan	Rest world	1000s of metric tons	% of total
Concrete additives	27	17	33	68	71	476	45
Animal feed binders	14	19	27	nil	nil	136	13
Dust control	19	50	2	nil	3	121	11
Agricultural dispersant	4	Small	12	1	nil	51	5
Drilling muds	5	Small	4	nil	1	40	4
Animal feed additives	9	nil	2	nil	nil	30	3
Other	22	14	20	31	25	199-220	19

(Source: Chemical Economics Handbook)

Lignin finds applications in a variety of different commercial outlets. These include:

Cement and concrete: Lignosulfonate salts provide plasticity and flowability to concrete. They compete with materials that provide longer initial set retardation, but are higher cost, such as gluconic acid, gluconates and superplasticizers. Powdered and liquid lignosulfonates can be used in wet-process Portland cement mills to increase the solids content of the raw slurries. Likewise, lignosulfonates are used to retard the set of neat cements in hot oil well applications.

Importantly, concrete manufacturers are currently scrambling to keep enough lignin in stock for these applications. Companies such as W.R. Grace and Master Builders use lignin products extensively in this application. Lignosulfonates for concrete applications can be as high as $4.00-5.00/gal as an aqueous solution.[52] A very rough calculation (8 lb/gal, assume 50% aqueous solution) gives a sales price for lignosulfonates of $1.00-1.25/lb. Secondly, Eastman Chemical distributes a material named Vinsol, which is also high in lignin and lignin-like materials. A patent search of Vinsol reveals that it has applications in several areas that overlap lignin; hence, the market is already in place to accept a Vinsol/lignin family of products. Importantly, Vinsol is a high-value product. As a concrete additive, Vinsol is $3.50-4.00/gal (sales prices), again in a concentrated aqueous form from the manufacturer. More broadly, lignin and Vinsol might be interchangeable in some applications, given the similarity of their chemical structure.

Animal feed pellets: Lignosulfonates are used in animal feeds, both as a binder for the pellets and as a diluent for molasses. They are worth around

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52 Tom Pello, Master Builders Denver sales representative, personal communication. Data subject to confirmation.

$0.05/lb. As a binder, the lignosulfonate may not exceed 4% of the finished pellets or flake grains. Likewise, the moisture content of the lignosulfonates may not exceed 6% by weight for spray-dried powder, or 50% by weight for liquid applications. Yeast solubles, animal glue, cereals and potatoes have replaced lignosulfonates in some pellet formulations.

Animal feed molasses additives: About 25 x 10^3 tonnes of lignosulfonates, primarily as calcium and sodium salts, were used in this application in 2001. Lignosulfonates are added to lower viscosity of the molasses mixture to allow easier transport and handling. The U.S. Food and Drug Administration (FDA) has approved inclusion of 11% lignosulfonate solids in molasses blends.

Road binder/dust control: A significant advantage of this market is that no chemical modification is required of the lignosulfonate liquor. The perceived environmental advantages of lignosulfonates over conventional road binders, such as calcium chloride, should provide opportunity for increased market share. For this application, concentrated crude spent sulfite liquors containing lignosulfonate are used without further purification. The spent solutions are concentrated and optionally blended with a surface-active ingredient. The application of such spent liquors appears limited to dust abatement. Typical amounts used for road dust are 1-2 gal of 25% solids solution per square yard. For mining use the application is 1-2 gal of 45% solution per ton of ore. When blended with surface active ingredients, these solutions can be applied as foams with low usage levels.

Pesticides: The U.S. market consumed about 11 x 10^3 tonnes of lignosulfonates for this application in 2001. Lignosulfonates are currently used as a dispersant for both wettable powder . water-dispersible granule or dry-flowable and suspension concentrate pesticide products. The dry-flowable application once had the greatest opportunity for increased market penetration because two to three times as much dispersant is required compared to wettable powders. However, the major players in the agrichemical industry such as Syngenta and Bayer CropScience are reemphasizing suspension of flowable products. An overall reduction in pesticide use is anticipated due to the increased efficacy of pesticides and to integrated pest management.

Oil well drilling muds: Lignosulfonates help provide desirable rheological properties to drilling muds at moderate conditions (high pressures and temperatures up to 177°C). Before 1992, the market share for chrome and ferrochrome lignosulfonates was on the order of 80%. However, lignosulfonates have recently lost considerable market share to water-based nonionic and cationic polymers. Oil well applications frequently command prices as high as $1.00/lb for the proper lignin derivatives. This presents an interesting application because some fairly high-valued lignin derivatives modified to improve lubricity, heat stability, dispersability (surface activity), and rheological properties fit into this application. Selling prices of $1.00 -

$2.00/lb or more for specialty lignin derivatives can be tolerated for drilling mud applications.[53]

Adhesives, resins and binders: Foundry casting and molding resins take advantage of the water adsorption, dispersing, adhesion and lubricating properties of lignosulfonates. The same is true with animal feed pellets. However, despite considerable R&D effort and the positive experience of Georgia Pacific, lignin adhesives are not a large market player. The Karatex process, developed by the Finnish Pulp and Paper Institute, has shown that a high-molecular weight fraction of kraft lignin can be used to displace up to 70 % of the phenol required for phenol-formaldehyde (PF) resins.[54] At this high level of displacement, curing times were somewhat lengthened. However, the bonding strength was comparable to pure PF resin. The PF resin market is fairly substantial with more than 800 x 10^6 lb consumed annually for bonding and adhesives applications. PF resins used in electrical, household, and automotive molding compound applications could provide another opportunity. Although PF molding compounds are losing market share in automotive applications due to increased heat resistance requirements, this is still a reasonably sized market at 90 x 10^6 lb/yr. For lignin, the opportunity for increased market share in either market lies in improved reactivity and in better heat resistance, either as a function of the lignin source or through chemical alteration.

Wallboard: Lignosulfonates have long been used as dispersant and water reducers in wallboard manufacture. Typically, 1-3 lb of lignosulfonate solids are added to a gypsum wallboard formulation per 1000 ft of ½-inch wallboard. They compete with synthetic surfactants (e.g., sulfonylated and hydroxymethylated naphthalenes) mainly on cost performance rather than inherent effectiveness.[55]

Dispersants: The charged, polyelectrolyte nature of lignosulfonates makes them surface-active. They are effective dispersants (solids in water dispersion). This behavior is rationalized by electrokinetic action of the negatively charged lignin transferring charge to the solids causing mutual repulsion of the solids. This feature may be largely traceable to physical adsorption on the solid surfaces. The net result is stabilized suspensions and reduced viscosity. However, lignosulfonates are not effective at creating true liquid – liquid emulsions unless modified in some manner.

Emulsifiers and wetting agents: In a manner analogous to dispersions of solids in liquids, lignosulfonates are able to stabilize oil-in-water interactions (liquid in liquid dispersion) especially when modified by hydroxymethylation,

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53 Personal communication with industrial representatives.

54 Kilpelainen, H., Forss, K., Fuhrmann, A., Wood Panel Prod. Lab., Tech. Res. Cent. Finland, Helsinki, Finland. Proc. IUFRO Conf. Wood Gluing (1976), Meeting Date 1975, 79-91; Publisher: U. S. Forest Prod. Lab., Madison, Wis.; M. Frank, Use and Value of Reactive Lignin New York State Energy Research and Development Authority Report, NYSERDA 89-2, March 1998.

55 Northey, R.A. in Chemical Modification and Usage of Lignin, Kluwer Academic Press, New York, Hu, T. H. ed., Kluwer Academic Press, New York (2002), Chapter 8.

carboxylation and aromatic ring sulfonylation. Most lignosulfonates reduce the tension at the oil - water interface. They also adsorb at the solid-liquid interface and therefore help facilitate wetting by conventional surfactants. Their rigid structures in combination with their polyelectrical properties make them excellent rheology-modifying agents for water-based systems.

Agglomerants: When lignosulfonates become wet they develop adhesive and agglomerating properties arising from their capacity to absorb and retain water, making them useful additives for solids that lack sufficient self-adhesion properties.

Chelants: Sodium, ammonium and calcium lignosulfonates have sequestering properties useful for micronutrient and leaf mold applications because they promote metal ion transport. As such, soil amendments containing lignosulfonates formulated with added micronutrients are in use. They are also particularly good at sequestering aluminum(III) ions, thus are useful for preventing or retarding the severe negative effect on plant growth induced by free aluminum in soil. Lignin's metal adsorption characteristics make it a likely competitor to conventional chelating agents such as aminopolycarboxylates. The most common chelants have a market of 165 x 10^6 lb/yr and annual growth of almost 5%. The pulp and paper industry is one of the major consumers of such chelants (40 x 10^6 lb/yr) for bleaching, de-inking, scale inhibition, and hydrogen peroxide transport stabilization. The growth of this segment is at least 10% annually. Water treatment is another area where lignin could prove applicable. More than 30 x 10^6 lb/yr of chelants are consumed in boilers, cooling water systems, evaporators and heat exchangers for applications such as scale inhibition. Aminopolycarboxylates currently sell for around $0.50-0.60/lb for liquids and as much as $1.90/lb for powders and crystals, making lignin-based chelants an attractive option.[56]

Leather treatment: Lignosulfonates combine or react irreversibly with proteins making them effective in preventing leather rot.

Anti-bacterial activity: Although its activity is weak, lignin has some ability to retard bacterial growth, and this may be of some importance in its use in food contact packaging and in leather treatments. Antibacterial activity of lignin may be one reason why lignin-treated wooden cutting boards are attractive in the food industry.

Lead acid batteries: Used as expanders and surface-modification agents. Lignosulfonates reduce polarization on the negative plate and improve battery life by reducing plate self discharge and sulfation when not in use.

Oil recovery: Reaction of lignosulfonates with fatty amines can produce an oil-soluble product with increased surface activity.[57] A 3:1 lignin:amine

56 Chemical Economics Handbook, Chelating Agents, SRI International.

57 DeBons, F.E., Whittington, L. E. J. Petroleum Sci. Eng., 1992, 7.

charge ratio is used to produce a 1.7:1 lignin:amine oil soluble product. This product can than be substituted for the oil soluble petroleum sulfonate, the most expensive component in the surfactant system. When the lignin-based surfactant is blended with water-soluble surfactants in brine, tertiary oil recovery can approach levels obtained with the petroleum sulfonate surfactant system. Kraft lignins did not prove as amenable as the lignin:amine ratio was about one-third that of the lignosulfonate product. The petroleum-based oil-soluble component costs on the order of $1.00/lb. With lignin costs being minimal and tallow amine costs on the order of $0.65/lb, there is opportunity for a competitive, renewable-based surfactant replacement system with an overall savings potential of as much as 46%

Water treatment: Lignosulfonates are used as dispersants and scale-deposit inhibitors for boiler and cooling tower water treatment.

Industrial cleaners: Dispersant qualities, mild surfactant qualities and ion-complexing ability make certain lignosulfonates a choice for industrial cleaning formulations to remove dirt particles and greases.

Emulsion stabilizers: Lignin, when modified by oxidation, hydroxymethylation or aromatic ring sulfonylation is used to stabilize emulsions.

Carbon black, inks and azo pigments: Lignosulfonates act as dispersants and grinding aids for carbon black, inorganic brown, grey and black pigments, as well as some organic pigments.

Dyestuffs: Lignin is used as a dispersant, extender, protective colloid, or as grinding aids.

Micronutrients: Lignosulfonate complexed with metal ions such as iron, calcium, copper, manganese, zinc, and magnesium are used as plant nutrients.

Fertilizers: Lignosulfonates that have been oxoaminated to as much as 30% total N are used as fertilizers.[58]

Bricks, refractories and ceramic additives: Lignosulfonates are used to improve plasticity, green strength (the ability of an incompletely cured material to undergo removal from the mold and handling without distortion) and molding properties; that is, faster production and fewer voids in production parts.

Ore processing: Lignosulfonates are used as floatation and separation aids.

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58 Japanese patent JP 2001206792 A2 and German patent DE 4308951; Fischer, K.; Schiene, R. in Chemical Modification and Usage of Lignin, Kluwer Academic Press, New York, Hu, T. H. ed., Kluwer Academic Press, New York (2002), Chapter 10.

Kitty litter: Lignosulfonates are used as a biodegradable alternate to clumping clays.

Commercial lignosulfonates may also be further modified before use to alter the dispersing, binding or complexing properties required for particular applications. Examples of modification chemistries and the resulting structural modifications are found in Table A.10.

Table A.10 – Lignosulfonate Modification Processes

Chemical processes	
Sulfonation	Chain extension
Sulfoalkylation	Crosslinking
Desulfonation	Graft polymerization
Amination	Acrylate grafting
Carboxylation	Depolymerization
Hydroxymethylation	Ion Exchange
Esterification	Desaccharification
Etherification	Additional formulation / blending

Past Commercial Lignin-Based Products

Commercial use of lignin-based materials was reviewed in 1999.[16] The findings reported in the review correlate well with our analysis based on personal contacts, interviews and data found on the websites of lignin producers. Another resource is the Lignin Institute, a nonprofit trade association of manufacturers and suppliers of lignin products, and from lignin producers. Lignin uses have been generally limited to applications in which the bulk properties such as solubility, surface activity and solids content are acceptable or important.

The following uses, once practiced in reasonably large scales, are no longer competitive with petroleum-based technology and have been discontinued with the exception of one vanillin plant in Norway and China. Volatility in petroleum feedstock prices and new lignin separation and conversion technology could have an impact on the economic viability of small molecular weight products, like these below, from future biorefineries (Figure A.19).
- Phenolics by alkaline hydrolysis
- Vanillin production by mild oxidation in alkaline conditions
- Production of dimethyl sulfide/sulfoxide by reaction with sulfur then oxidation (not part of our future consideration)
- Organic acids by strong oxidation include: benzoic, toluic, methoxybenzoic, acetic and formic acids.
- Lignin hydrogenolysis to phenols and aromatic hydrocarbons (Noguchi process 1959-1966, Crown-Zellerbach 1966, Hydrocarbon Research Inc. "Lignol Process 1960's - 1983)

- Recovery of mixed formaldehyde + substituted phenol stream for plywood and oriented strand board manufacture.
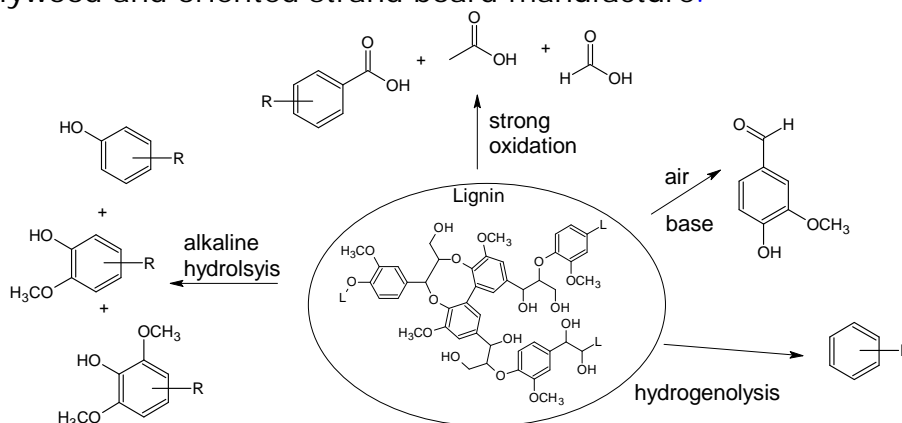

Figure A.19 - Previous Commercial Lignin Transformations

Georgia-Pacific has extensive experience in the commercial production of lignin-based PF adhesives and for a time had a 4000-5000 tonne/yr market on the west coast, with a longer-term projected market of 25,000 tons/yr. Loss of this capacity later forced Georgia-Pacific to focus on traditional PF resins at the expense of lignin-based products. The projected cost in this application alone was $0.13-$0.15/lb, already 4-5 times higher than fuel value.

Lignin Toxicity

Lignin exhibits a generally low level of toxicity. Extensive animal testing as well as direct human experience has shown that all organic solvent-free lignin, especially kraft lignin and lignosulfonates, are essentially nontoxic to both animals and humans. LD_{50} values greater than 12 g/kg of body weight have been reported.

Kraft lignin and lignosulfonates have gained FDA approval for safe use in manufacturing and use in a wide variety of food-grade applications. These include pesticides (21CFR 182.99, 40 CFR 180.1001, and 21 CFR 172.715), in boiler water food grade steam (21 CFR 173.310), food packaging (21 CFR 176.170, 178, 3120, 176.120, and 176.180 and others) and in animal food (21.CFR 573.600). This is not surprising because lignin is a significant component of all vegetables and whole grains.

Commercial Lignin Suppliers

The following companies are suppliers of lignin products:

LignoTech USA. As part of the Borregaard group, LignoTech is the world's largest manufacturer of lignin. They market binding and dispersing agents derived from lignin and lignosulfonate. Markets include: animal nutrition (pellet binders, bypass proteins); additives for ceramics, concrete and gypsum board; dispersing agents for agro chemicals, battery expanders, carbon black, dye baths, dyestuffs and water treatment; dust control for roads and industrial dusts; binders for carbon black, fertilizers, limestone and mud dispersants; and plant nutrition (humates and micronutrients).

Tembec. A leader in sulfite pulp sector, Tembec produces lignosulfonates. They claim a total capacity of 570,000 tonnes/yr from their three plants in Europe and North America. Product uses include dispersants, binders and chelators.

Fraser Paper. Fraser prepares lignosulfonates completely from hardwoods (birch) for applications in animal feed pellets, dust control, brick and refractory production, concrete admixtures, and binders.

MeadWestvaco. MeadWestvaco manufactures specialty lignin and lignosulfonate along with tall oil fatty acids and their derivatives. They are the only U.S. producer of non-sulfonated kraft lignin. They also manufacture some aromatic ring sulfonated and hydroxymethylated lignin and have the technical capacity to produce other specialty products; for example, propoxylated lignin polyols. Their lignins find use as dispersants additives for cements and animal feeds, components of oriented strand and particle board, wax emulsions, lead acid batteries, dyes and pigments, ceramics, refractories and concrete.

Northway Lignin Chemical. Northway makes binders and binder systems for agglomeration. Specialty binders include sulfur-free kraft lignin, organic binders, emulsifiers, stabilizers, dispersants, and liquid or powder agglomeration.

KMT Lignin Chemicals. KMT manufactures lignosulfonates for binding and dispersing applications. Their dispersants are used in concrete admixtures, dust abatement, oil well drilling muds, leather tanning, ceramics, dyestuffs, insecticide sprays and pipeline transport (increasing the solid content in slurries). Binder uses include wallboard and animal feed additives.

Melbar. Melbar makes lignosulfonates exclusively from pinewood and markets them as agglomerants, dispersants, emulsifiers and wetting agents, chelating agents, and animal hide treatments.

Lennox Polymers LTD. Lennox is unique from the other lignin suppliers in that it is directly involved with polymers. They have developed technology related to formaldehyde-free resins and adhesives based on lignin from black liquor. Historically, their core business has been with foundry resins and wood products such as chips, laminates and veneers (wood binding resins).

They are attempting to move into higher-performance specialty resins including tooling resins, urethane molding resins, thermoplastic resins polyester molding resins, and traction products. Lennox has licensing agreements with Bakelite AG (Germany) and a Japanese consortium of foundries. A winter tire traction product contains a Lenox lignin product. At least one Japanese company is reported to offer similar products. Lennox's winter traction product and lignin's use in lubricants and dispersing aids illustrate the range of properties that can be derived from lignin.