

Final Report: Investigation of Catalytic Pathways for Lignin Breakdown into Monomers and Fuels

October 2010

Jeffrey Gluckstein, Michael Hu, Michelle Kidder, Joanna McFarlane, Chaitanya Narula, Matthew Sturgeon

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge.

Web site <http://www.osti.gov/bridge>

Reports produced before January 1, 1996, may be purchased by members of the public from the following source.

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Web site <http://www.ntis.gov/support/ordernowabout.htm>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source.

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Web site <http://www.osti.gov/contact.html>

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Energy and Transportation Sciences Division

**INVESTIGATION OF CATALYTIC PATHWAYS FOR LIGNIN BREAKDOWN
INTO MONOMERS AND FUELS**

Jeffrey Gluckstein, Michael Hu, Michelle Kidder, Joanna McFarlane, Chaitanya Narula, Matthew
Sturgeon

October 2010

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

| | Page |
|--|------|
| LIST OF FIGURES | v |
| LIST OF TABLES | vii |
| ACRONYMS | ix |
| ACKNOWLEDGMENTS | xi |
| EXECUTIVE SUMMARY | xiii |
| ABSTRACT | 1 |
| 1. INTRODUCTION | 1 |
| 1.1 CONCEPT UNDER REVIEW | 3 |
| 2. THERMODYNAMIC ANALYSIS | 5 |
| 2.1 CRITERIA FOR PROCESS COMPARISONS | 5 |
| 4.1.1 Lignin Conversion Process Overviews | 5 |
| 4.1.2 Baseline Lignin Value | 6 |
| 2.2 LIGNOCELLULOSIC BIOREFINERY | 7 |
| 4.2.1 Process Analysis | 8 |
| 4.2.2 Suggested Process Improvements | 10 |
| 2.3 HYDROTHERMAL ROUTE | 11 |
| 4.3.1 Energy and Economic Analysis of Hydrothermal Route | 13 |
| 4.3.2 Hydrothermal Treatment of Heavy Oil | 14 |
| 4.3.3 Suggested Process Improvements | 14 |
| 2.4 KRAFT LIGNIN PYROLYSIS | 15 |
| 4.4.1 Process Analysis | 16 |
| 4.4.2 Suggested Process Improvements | 17 |
| 3. EXPERIMENTAL | 19 |
| 3.1 MATERIALS | 19 |
| 3.2 ANALYSIS | 19 |
| 3.3 BORON TRIBROMIDE TREATMENT | 21 |
| 3.4 RHODIUM CATALYST TREATMENT | 21 |
| 3.5 ELECTROCATALYTIC HYDROGENATION | 21 |
| 4. RESULTS | 24 |
| 4.1 BORON TRIBROMIDE ACIDOLYSIS | 24 |
| 4.2 HOMOGENEOUS HYDROGENATION | 24 |
| 4.3 ELECTROCATALYTIC HYDROGENATION | 25 |
| 5. NANOMANUFACTURING IN LIGNIN CONVERSION TO FUELS | 28 |
| 5.1 PRODUCTION | 28 |
| 5.2 USE | 28 |
| 5.3 FATE | 28 |
| 6. CONCLUSIONS | 29 |
| 7. REFERENCES | 30 |

LIST OF FIGURES

| Figure | | Page |
|--------|--|------|
| 1 | High level flow sheet for lignin isolation, decomposition, and conversion into value added feedstocks | 4 |
| 2 | Process overview for the conversion of Organosolv lignin to alkylphenols | 8 |
| 3 | Schematic of electrochemical cell for lignin conversion to phenolic compounds using a solid acid proton transport membrane | 11 |
| 4 | Process overview for the conversion of pyrolytic lignin to mixed fuel | 12 |
| 5 | Process overview for the conversion of Kraft lignin to simple aromatics | 15 |
| 6 | Inorganic membrane developed at ORNL for separation of nanoscale particles and molecules | 18 |
| 7 | Sample analysis flowsheet | 20 |
| 8 | Schematic of electrocatalytic hydrogenation apparatus | 22 |
| 9 | Palladium catalyst deposited on carbon foam electrode before use in electrocatalytic cell | 22 |
| 10 | X-ray photoelectron spectroscopy results for the electrode shown in Fig.9 | 23 |
| 11 | Production of hydrogen during ECH of syringic acid | 25 |
| 12 | Hydrogen production from ECH of lignin..... | 26 |
| 13 | UV absorption of the ECH products of phenylethylphenylether (PEPE) | 27 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| 1 | Steps involved in processing lignin | 11 |
| 2 | Material and energy requirements for the conversion of lignin..... | 10 |
| 3 | GC detectable products from the hydrocracking of pyrolytic lignin | 13 |
| 4 | Product yields as wt.% of total product | 16 |
| 5 | Energy required for the pyrolysis of 1 kg lignin..... | 17 |
| 6 | Recovery of lignin and products in separated fractions after acidolysis..... | 24 |

ACRONYMS

| | |
|------|--------------------------------|
| ECH | electrocatalytic hydrogenation |
| FID | flame ionization detection |
| GC | gas chromatography |
| HDO | hydrodeoxygenation |
| HP | Hewlett Packard |
| MS | mass spectroscopy |
| ORNL | Oak Ridge National Laboratory |
| PEPE | phenylethylphenylether |
| UT | University of Tennessee |
| UV | ultraviolet |

ACKNOWLEDGMENTS

This research was provided by the Department of Energy's Office of Energy Efficiency and Renewable Energy's Industrial Technologies Nanomanufacturing Program, carried out at the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under contract #DE-AC05-00OR22725.

EXECUTIVE SUMMARY

Recently, Oak Ridge National Laboratory (ORNL) has investigated the catalytic conversion of lignin to small aromatic compounds of commercial value as building block feedstocks for commodity chemicals. However, even though success has been achieved in the laboratory, methods for processing lignin still pose technological barriers that need to be assessed before scale up to a commercial plant. This concept-definition project investigated the use of nanocatalysts to facilitate the breakdown of refractory organics from unconventional sources: primarily from lignin, but also bitumen and oil shale into feedstocks that can be used for fuel and for the chemical industry. Lignin conversion requires a breakdown into monomers as well as hydrogenation and deoxygenation of the methoxy and hydroxyl substituents on the aromatic framework. The goal is preserve the aromatic rings of the lignin polymer while stripping the molecule of oxygen, yet preventing repolymerization into a more refractory char.

The project was undertaken in two parts:

- The experimental evaluation of a number of different catalytic pathways for the decomposition of lignin into small molecules,
- The evaluation of flowsheets for lignin decomposition in terms of thermodynamic efficiency.

It was expected that lower temperature conversions and more rapid processing could be gained from the use of nanocatalysts in lignin breakdown. In addition, if high temperatures can be avoided, it is expected that aromatic moieties will remain intact and a thermodynamic advantage can be gained relative to syngas production and reconstitution of lignin, along with less char formation. Flowsheets to achieve conversion under less extreme conditions were compared with conventional pyrolysis, to identify areas where catalysis could play a major role in increasing the feasibility of lignin conversion.

The experimental scope of work compared heterogeneous catalysis with homogeneous catalysis for lignin conversion efficiency. The methods tested included:

- BBr_3 room temperature decomposition of lignin in CH_2Cl_2
- Oxo-Rh cluster catalyst hydrogenation of lignin in aqueous solution
- Pd-catalyst on alumina electrocatalytic decomposition of lignin
- Pd-catalyst reduced on carbon foam electrocatalytic decomposition of lignin

The scope of experiments gave a realistic understanding of the issues related to lignin conversion to fuels. Palladium nanocatalysts were synthesized fairly readily. However, the catalysts need to be supported on a framework that can be separated from the lignin to prevent posing an additional separation issue in lignin conversion.

In addition to the experimental work, a thermodynamic analysis was carried out for the conversion of lignin to fuels through three separate pathways: via conventional pyrolysis, in a lignocellulosic biorefinery, and through a hydrothermal route. It was determined that in any analysis of lignin conversion, boundaries must be clearly established around the system of interest, and alternative uses for the feedstocks and products must be considered along with the evaluation of the fuels produced. One of the key factors in the feasibility of lignin conversion is the source of the hydrogen used in the process, needed to increase the carbon-to-hydrogen ratio in each of the processes. The thermodynamics of hydrogen production also has an impact on the overall energy balance of the system.

It is expected that advances in the use of economical catalysts, such as clay minerals, can be coupled

with the selectivity advantages posed by nanomaterials to greatly enhance the efficiency and economics of the processing of refractory materials such as lignin. However, considerable research is needed before this goal can be achieved. In particular, the issues identified in this conceptual study included:

- Feedstock variability and solubility
- Mass transfer of lignin to active sites for catalytic breakdown
- Targeting of desired products
- Repolymerization
- Catalyst support optimization
- Catalyst integrity and activity under harsh conditions
- Cost and production of hydrogen feedstock
- Separations of desired products from unwanted byproducts and salts

ABSTRACT

Lignin is a biopolymer that comprises up to 35% of woody biomass by dry weight. It is currently underutilized compared to cellulose and hemicellulose, the other two primary components of woody biomass. Lignin has an irregular structure of methoxylated aromatic groups linked by a suite of ether and alkyl bonds which makes it difficult to degrade selectively. However, the aromatic components of lignin also make it promising as a base material for the production of aromatic fuel additives and cyclic chemical feed stocks such as styrene, benzene, and cyclohexanol. Our laboratory research focused on three methods to selectively cleave and deoxygenate purified lignin under mild conditions: acidolysis, hydrogenation and electrocatalysis. (1) Acidolysis using boron tribromide was undertaken in CH_2Cl_2 at room temperature. (2) Hydrogenation was carried out by dissolving lignin and a rhodium catalyst in 1:1 water:methoxyethanol under a 1 atm H_2 environment. (3) Electrochemical conversion of lignin dissolved in a solution of 1M NaOH(aq) was carried out at a catalytic palladium cathode using hydrogen from the electrolysis of water. In all of the experiments, the lignin degradation products were identified and quantified by gas chromatography mass spectroscopy and flame ionization detection. Yields were low, but this may have reflected the difficulty in recovering the various fractions after conversion. Acidolysis resulted in under 1% yield of bromocyclohexanes. The homogeneous hydrogenation of lignin showed fragmentation into monomers, while the electrocatalytic hydrogenation showed production of polyaromatic hydrocarbons and substituted benzenes. In addition to the experiments, promising industrial scale pathways for the conversion of lignin were assessed. Three conversion methods were compared based on their material and energy inputs and proposed improvements using better catalyst and process technology. A variety of areas were noted as needing further experimental and theoretical effort to increase the feasibility of lignin conversion to fuels. In particular, the thermodynamics of hydrogen needed for the conversion of lignin played an important role in the feasibility of the process.

1. INTRODUCTION

Biomass derived fuels have the potential to reduce the dependence of the US on foreign oil as well as reduce green-house gas emissions associated with the burning of fossil fuels (Perlack et al. 2005). However, biomass production, harvesting and conversion to fuels is energy intensive. While the first two issues are beyond the scope of this project, the conversion may lend itself to using technologies taking advantage of nanocatalysis to: 1) decrease the energy cost; 2) use primarily cellulosic biomass or non-food natural oils and resins as feedstocks; 3) produce fuel at a high yield from incoming dry biomass; and 4) produce fuels with physical and chemical properties, as well as costs, that closely match those of petroleum-derived fuels and are fully compatible with petroleum streams and infrastructure. It is also desirable that co-products be minimized in order to maximize yield and reduce process energy requirements.

Woody biomass is the highest-volume feedstock for production of infrastructure compatible fuels. Additionally, some biomass forms, such as grasses, contain materials, such as waxes, cutins, resins, rosins, long chain fatty acids, and extractives which may also be of value as feedstock constituents. The high molecular weight polymers that constitute plant material can be classified as cellulose, based on six carbon sugars; hemicellulose, based on pentoses; and lignin, aromatic rings connected

through ether, C-O-C, linkages (Lapierre et al. 1999). These components have different end uses and so must be separated and broken down in a biorefinery before conversion to the final feedstock or product. Because lignins and hemicellulose together constitute 40-50 wt.% of woody biomass, it is important to use these materials as feedstocks for fuels.

Lignin, a polymer with a molecular weight of about 2500, is available in extremely large quantities as it comprises 15-30 wt.% of wood, <10 wt.% grass, and 25 wt.% switchgrass. One billion tons of woody biomass would provide the equivalent of 6×10^{15} Btu (6 quads) more lignin than currently needed for process heating (or 100 M tons). As well as pulp-derived lignins, biomass hydrolysis liquors are gradually becoming available as biorefineries develop. Lignin can be recovered together with associated carbohydrates using both standard industrial and an advanced ORNL-developed process. Lignin from pulping and biomass liquors is typically recovered as a highly impure material mixed with hemicellulose and other constituents, such as pine oils, extracted from wood and biomass. Current commercial practice indicates that >30 million tonnes per year (~40% of process inventory) of impure lignin can be recovered from commercial pulping liquors in the US (Chiang 2002). As biomass becomes a fuel feedstock, biorefineries are expected to increase the available amount of this material.

ORNL has developed technologies for recovering and separating a mixture of hemicellulose and lignin under conditions which minimize impact on pulping processes. The ORNL process (Compere et al. 2005) permits recovery of a gelatinous high-hemicellulose, high-lignin precipitate from alkaline (Kraft, soda anthraquinone) pulping liquors*. However, the technology does not take the process all the way from intact lignin to fuels, Fig. 1, the topic of the current report.

Lignin and related materials from pulping liquor and biomass hydrolysis are expected to be relatively low in cost because current practice and future designs treat them as low-valued fuels. The current value of lignin can be assessed by calculating the value of the heat produced when it is burned (\$40/ton), with 70% energy content of #2 fuel oil. By providing heat at pulp mills, lignin and hemicellulose already provide a reduction in fossil-derived greenhouse gas emissions well in excess of 50%. Mill balance constraints limit current processes to ~ 10% of the total lignin in pulping liquor (>80 million metric tons per year). However, to make the ORNL process economically viable, a low energy method for the separation of hemicellulose and lignin is needed, likely using an enzymatic or chemical hydrolysis of the gel precipitate containing these materials.

Recovered lignins are typically both sulfided from Kraft and sulphite processes (detrimental to catalysts) and contain large amounts of undesired materials (fiber, sand, inorganics), as well as hemicellulose. In addition, lignin composition, structure, and degree of impurity can vary depending on the biomass source and processing conditions. Filtration for removal of contaminants is typically difficult due to filter blinding by precipitated lignins and waxes. Previous experience has shown that this can often be alleviated through careful selection of filtration materials, flow rates, and low-volume chemical additives. An effective method for separating low salt, low sulfur lignins from the mix is desirable.

Concentrated lignin (after carbohydrate removal) is pitch-like (Botto 1987), and can make “coke” like material. However, lignin can also be a source of aromatics, plastics, and binders. High value chemicals increase viability of biorefinery. One million metric tons of lignin is currently commercially produced in pulp mills – but not for higher value-added products.

To be made into useful fuels and building block chemicals, the purified lignin has to be broken apart.

* The lignin and hemicellulose can be separated using enzymatic or chemical hydrolysis of the gel precipitate.

If done gently, the goal of this process is to produce phenols, cresol, resorcinol and hydroquinone precursors, requiring breaking apart ether linkages, and aromatic and aliphatic hydrocarbons, requiring decarboxylation, and demethylation of lignin rings. To retain the value-added aromatic character means avoiding high temperatures or extreme chemical environments.

1.1 CONCEPT UNDER REVIEW

The focus of this project is the use of nanocatalysts for ether cleavage and hydrogenation/deoxygenation of lignin. The chemistry of cleavage by clay-based nanocatalysts has been investigated and reviewed by a number of groups (Deville and Behar 2001, review by Nikalje et al 2000, review of clay activity Knifton 1998). The priority is to obtain biofuels that can be used as an additive or replacement for gasoline, value-added chemicals, or biodiesel-type methyl esters. Lignins can be used to make aromatics, naphthenics, short-to-long chain hydrocarbons, and branched alkanes, all of which are components of gasoline.

Acid-exchanged clay catalysts (monmorillonite) have been reviewed by Buchanan et al. (1997), with the advantage that these materials are layered to increase the surface area. The typical metal catalyst Ni-Co-Mo-W (less than 1 micron dia) is supported on the inorganic salt or clay (Stamires et al., 2006). The metal clay supported nano-catalyst, once prepared, is mixed with the hydrocarbon at 70-200°C. At those temperatures, the clay delaminates exposing the metal reactive sites and conversion reactions occur.

Microwave enhancement of ether cleavage has been investigated by Meshram et al. (1999), and enhancement of the activity of nanocatalysts in the decarboxylation of organics has been studied at ORNL. Photoassisted enhancement of ether cleavage in 2-phenoxybenzoic acid has also been studied (Katagi 1992, 1991). Reactions on clays can also be carried out in methanol at 40-50°C (Li et al. 1999)

Hydrogenation reactions have been catalyzed on ball-shaped Pd nanocatalysts in MCM-48 matrix substrate. The palladium domains are 38 nm across. The key advantage to this process is selectivity, where hydrogenolysis (ether cleavage) occurred much more quickly than hydrogenation of the olefin. This advantage was not seen with similar Pd/C or Pd/SiO₂ catalysts. The Pd nanocatalysts have been used to assist benzyl bromide addition (8 fold increase in rate) to produce primary alcohols, rather than secondary or tertiary alcohols (Lee et al. 2006).

This study investigated bench-scale conversion of lignin using three different catalysis scenarios, including one incorporating Pd adsorbed on alumina. In addition flowsheets for lignin breakdown processes were evaluated in terms of the thermodynamic efficiency of the process and areas for process improvement using nanocatalysts were identified.

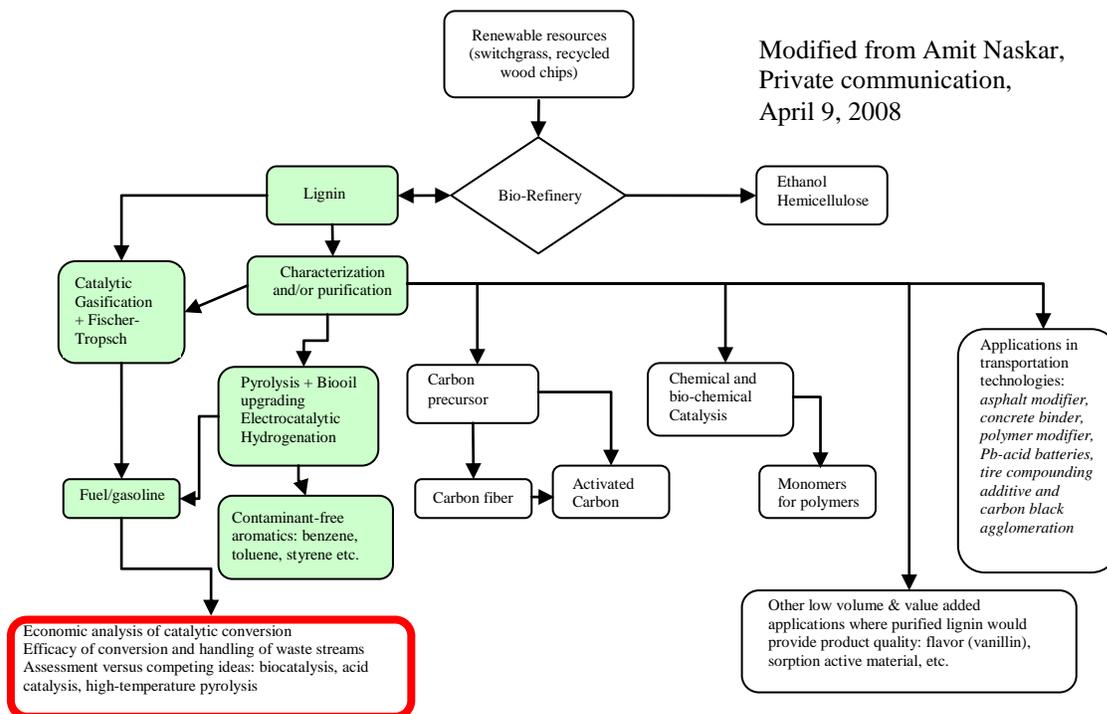


Fig. 1. High level flow sheet for lignin isolation, decomposition, and conversion into value added products.

2. THERMODYNAMIC ANALYSIS

An analysis of three very different pathways fed by three types of lignin was carried out to assess the state-of-the art in lignin conversion and whether the use of heterogeneous nanocatalysts could improve the processing. Lignin is currently burned in industrial processes, but its high aromatic content makes it a theoretically promising source for aromatic-based fuels and feedstocks. Lignin conversion to value added products has been subject to a number of excellent reviews, and it is upon this literature, as well as recent publications, that the processes were selected for analysis. The analysis includes consideration of thermodynamics of conversion and energy requirements. For each of the processes, improvements have been suggested as well as research activities to move the processes from bench-scale success to larger scale demonstration. This analysis is not meant to be comprehensive in terms of process, feedstock, or selected criteria. However, this work illustrates a path forward following pre-established goals of thermodynamic efficiency, selectivity, and feasibility.

2.1 CRITERIA FOR PROCESS COMPARISONS

Lignin comes from industrial processes such as wood pulping and cellulosic ethanol production. Separated lignin streams are burned for process heat and energy. Viable biorefinery methods to convert lignin into fuels and chemicals could significantly increase lignin's value from that of a fuel for combustion. Lignin is also present in the pyrolysis products of whole biomass, though this pyrolytic lignin is not currently industrially separated. Though raw biomass can be pyrolyzed to produce biofuels, the separation of biomass into cellulose, hemicelluloses, and lignin allows for more selective conversion of the purified components.

Assuming lignin will be available as a byproduct of current and foreseen industrial processes, the energy and material consumption involved in the production of lignin has not been included in the energy analysis of the lignin conversion processes. Standard pretreatment methods can produce a variety of lignin feedstocks. The examples included in this analysis include: Kraft lignin from pulping, Organosolv lignin, and the pyrolytic lignin component of bio-oil. Processes for the production of fuels must be both economically sound and consume less energy than the heating value of the final products. Miscibility and fungibility with current fuels are also considered. For the production of commodity chemicals, a comparison to current (2010) prices has been carried out.

The value of both fuel and chemical production pathways are compared to the current use of lignin for heat and power generation. Costs from plant construction, labor, maintenance, and operations are ignored as the analysis focuses on chemical and energy requirements, thereby highlighting these areas for further research. Technological limitations are identified and possible solutions are proposed, with special focus given to applications of nanotechnology.

2.1.1 Lignin Conversion Process Overviews

Regardless of the specific choice of treatment method, conversion of lignin to fuels or bulk aromatic chemicals requires the steps listed in Table 1, though they may not necessarily occur independently or in this order. The requirements of each of these steps must be considered when outlining technical and research needs for developing a feasible chemical process flowsheet.

Table 1. Steps involved in processing lignin

| | |
|---|---|
| Pre-treatment and Fractionation | Separation of biomass into lignin, cellulose and hemicelluloses or the separation of aromatics from processed whole biomass. Pretreatment may involve the removal of water, sulfur, alkali, or cellulosic impurities from lignin in order to prevent catalyst fouling. (Compere et al. 2005) The fractionation of biomass may also reduce the molecular weight or alter the chemical bond linkages in lignin. |
| Depolymerization | Ether and alkyl linkages between the aromatic groups in lignin must be cleaved in order to produce aromatic monomers. |
| Modification of functional groups | Reduction of methoxy, hydroxyl, or alkyl groups to produce chemicals with lower oxygen to carbon ratios while protecting aromatic groups is necessary to produce valuable commodity chemicals or fuels. Oxidative modifications can be used to produce fine chemicals such as vanillin (Tian 2010), but highly selective processes for food-grade or pharmaceutical chemicals will not be considered in this study. |
| Product and catalyst/solvent separation | Catalysts, solvents, and untreated lignin will need to be separated from the final reaction products. Several separation steps may be necessary throughout the lignin conversion process in order to obtain purified products. |

Processes used to produce biofuels must deoxygenate lignin and avoid the formation of polyaromatic hydrocarbons, essentially accelerating geological conversion processes which in nature take millions of years (Barth 1999). The production of fuels should be less energy intensive than conversion of lignin to specific aromatic chemicals, as less selectivity is required. Many processes have been developed for biomass and or fractionated lignin conversion to smaller molecules and have been reviewed in detail elsewhere (Zakzeski 2010). In general, the conditions for conversion to specialty chemicals are likely to be quite different from the production of fuel oil (Graham et al. 1994). For any process, there is a need to optimize chemistry, heat transfer, residence time, and quenching to form the desired product mixture.

2.1.2 Baseline Lignin Value

Lignin is burned along with other process byproducts in the pulp and cellulosic ethanol industries in order to produce heat and electricity. The value of any products from lignin must exceed the value of lignin for heat and power uses in order to be considered feasible, Equation 1.

$$Lignin\ Value\ Added\ Products\ \left(\frac{\$}{kg}\right) > Lignin\ HHV\ \left(\frac{MJ}{kg}\right) * Coal\ Price\ \left(\frac{\$}{MJ}\right) \quad (1)$$

The application of the formula to lignin higher heating values ranging from 21MJ/kg to 26MJ/kg leads to dollar values of lignin between \$0.035/kg - \$0.044/kg. Though this value is likely an overestimate because current boilers are better suited to coal than to lignin, it provides a baseline that valorization processes must surpass. The Energy Information Administration (Guey-Lee 2009) tracks

the price of fuels against which the cost of lignin upgrading can be compared. For instance, using lignin as a replacement for coal in boilers means that lignin must cost less than the very inexpensive coal price of \$1.78/MBtu (2006)[†]. However, if upgraded to vehicle fuel, the valorization of converted lignin needs to be compared with the cost of diesel, the retail price that has leveled off at about \$3.00/gallon over 2009-2010[‡]. Neither of these figures takes into account the environmental cost of fossil fuel burning and production of CO₂, which could raise the price of coal relative to biomass feedstocks.

Three pathways of lignin conversion to value added chemicals were compared.

1. Conversion of pure lignins from lignocellulosic biorefineries to phenols through hydrogenolysis and electrocatalytic hydrogenation
2. Upgrading of the lignin fraction of pyrolytic bio-oil to fuels via catalytic hydrocracking
3. Pretreatment and conversion of current industrial lignins (kraft or sulfite) to fuels using flash pyrolysis

The pathways analyzed in this paper were chosen in order to encompass a broad a range of lignin feedstocks and final products. Promising bench scale experimental results from the literature were used to determine process inputs and product yields, and so do not include issues with capacity and adaptation to commercial scale.

2.2 LIGNOCELLULOSIC BIOREFINERY

Separating lignocellulosic biomass into its primary components permits the fermentable sugars in biomass to be upgraded separately from the lignin, allowing for more selective and efficient upgrading of both product streams (Zhu et al. 2010). Lignin produced from specialized fractionation methods such as organosolv pulping or steam explosion is free from process sulfur contamination and retains much of its native chemical structure, though its molecular weight is reduced to roughly 1000g/mol (Binder et al. 2009). Purified lignin is an ideal candidate for selective catalytic processes.

The pathway proposed in Fig. 2 for the conversion of biomass to phenolic chemicals involves depolymerization of a purified lignin stream using electro-catalyzed hydrogenolysis and the reduction of lignin monomers and dimers by electrocatalytic hydrogenation. The raw lignin and lignin products are in solution throughout the process.

[†] <http://www.eia.doe.gov/neic/infosheets/coalprice.html>

[‡] <http://tonto.eia.doe.gov/oog/info/gdu/gasdiesel.asp>

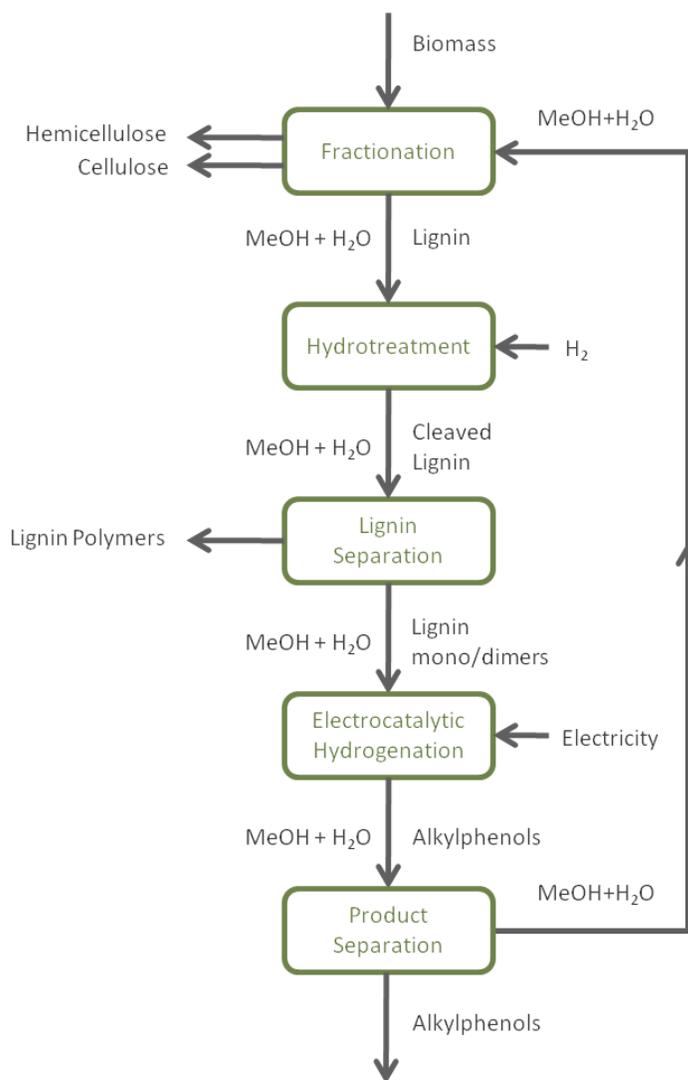


Fig. 2. Process overview for the conversion of Organosolv lignin to alkylphenols

2.2.1 Process Analysis

This process assumes that a lignin stream is available from a lignocellulosic biorefinery such as a cellulosic ethanol plant, though integrated biorefineries to produce valuable products from all the components of biomass do not yet exist. The choice of delignification process can have a large overall effect on the energy balance of the process as a whole. Yields of fermentable sugars for the production of ethanol per unit of energy used in separation have been published (Zhu and Pan 2010), and similar efforts should be devoted to assessing the overall value of all products produced from biomass feedstocks.

High purity lignin separated from biomass using methods such as the organosolv or steam explosion processes can be fed into a depolymerization step without being separated from the fractionation solvent (e.g., Kleinert and Barth 2008). For the thermodynamic analysis, the solvated lignin output was assumed to be 6:1 mass ratio of solvent:lignin dissolved in 1:1 volume ratio of ethanol:water.

The energy and material analysis of the hydrogenolysis step was based on a method published by Yan and coworkers in 2009 to produce phenolic monomers and dimers from purified lignin using a noble metal catalyst supported on carbon under hydrogen in a near critical dioxane and water mixture (200°C, 7 MPa) with 1 wt.% phosphoric acid. Their process resulted in lignin monomer yields of up to 46.4 wt.%, suggesting that nearly all of the ether linkages in lignin were broken while the alkyl linkages were left intact.

The material and reagent usage during hydrogenolysis was estimated by assuming that one molecule of hydrogen was necessary to cleave each ether bond and assuming that 70% of the linkages in the lignin were ether bonds. Only the monomers from the cleavage of lignin were considered valuable products, while dimers and oligomers were fed into the waste stream. This represented a conservative approach as many of these partially reacted materials could be reintroduced into the process stream. A model monomer with the formula $C_9O_{2.34}H_{8.05}(OCH_3)_{1.07}$ was assumed for the energy calculations, with bond energies coming from Beste and Buchanan (2009). Experimental results suggest that the activity of used catalysts in hydrogenolysis was not significantly reduced, so the deactivation of the catalyst was assumed to be negligible (Yan et al. 2009) The energy usage during hydrotreatment was assessed by determining the heat necessary to raise the temperature of the solvents, lignin, and hydrogen from 293K to 473K and the work necessary to compress the hydrogen to 6.5 MPa.

A subsequent step to separate unreacted lignin oligomers from monomers and dimers would likely be necessary following hydrotreatment. This fraction, expected to comprise about 50% of the total mass of lignin, could be recycled and burned for process heat. Although the energy consumption for such a step was not considered in this analysis, a membrane separation process based on size exclusion could potentially be used with very low energy penalty.

The monomers and dimers produced during hydrogenolysis could be reduced using electrocatalytic hydrogenation to produce alkyl phenols. Electrocatalytic hydrogenation has been shown to selectively convert lignin model compounds to reduced phenolic compounds (Mahdavi et al. 1997 and Cyr et al. 2000). For the published reaction, lignin model compounds were dissolved in 1M NaOH and adsorbed hydrogen atoms for reduction and deoxygenation were generated on a carbon cathode loaded with Pd/Al₂O₃. A similar method is proposed to convert lignin monomers and dimers using ethanol and water as the solvent. Cleavage of methoxy groups from the lignin monomers results in the production of methanol. The products were assumed to be ethyl and propyl phenols as described by Cyr and colleagues (2000).

Energy consumption was assessed by assuming that a voltage of 2.2V is necessary for the production of hydrogen by the electrolysis of water. Ideally, electrolytically generated protons adsorbed on the catalytic palladium are consumed in the reduction of lignin rather than in the formation of hydrogen gas.

After electrocatalytic hydrogenation, the solvent and lignin oligomers need to be separated from the alkylphenols. Fractionation could be done through distillation, solvent extraction, or by acidification of the aqueous phase to promote phase separation and formation of an organic layer. Because this area needs much more research, the energy required for separation was not assessed. The unconverted lignin oligomers could be used to produce process heat. Alternatively, if a higher partial pressure of hydrogen is needed to achieve good product yields, the unconverted lignin could be gasified to produce hydrogen for the hydrogenolysis step.

The overall material and energy consumption is given in Table 2 below assuming 100% conversion of the lignin to alkylphenols. The energy and phosphoric acid consumption in the hydrogenolysis step is largely dependent on the amount and type of solvent used, while the ratios of hydrogen consumption,

electrical energy use, and methanol production to alkylphenols are unlikely to change significantly with changes in processing technologies that follow this pathway.

Table 2. Material and energy requirements for the conversion of lignin

| Hydrogenolysis (per kg phenol produced) | | Electrocatalytic Hydrogenation (per kg phenol produced) | |
|--|-------|--|----------------|
| Hydrogen (g) | 23 | Methanol (g) | 180 (produced) |
| Phosphoric Acid (g) | 217 | Electrical Energy (kJ) | 7800 |
| Energy (kJ) | 11600 | | |

Once the lignin has been broken down into phenols, the chemistry of conversion of these compounds to non-functionalized aromatics and polymers is well known (Vermeiren and Gilson 2009). For instance, phenols can be selectively hydrogenated to cyclohexanone (desired for adipic acid production) and cyclohexanol (Shore et al. 2004). Shore used Pd-Yb/SiO₂ to give cyclohexanone yields with a selectivity of up to 68 % at 423K (achieving a 50 % conversion over 2 h) in a plug-flow reactor. However, in this case the fractional phenol conversion was found to be inversely proportional to production of the desired ketone versus other products. The authors also investigated Ni as a catalyst, and found it to generate a third of the selectivity and yield of Pd.

2.2.2 Suggested Process Improvements

While this process is theoretically capable of producing significant yields of phenolic chemicals, the technology is relatively unproven and significant gains in energy and material efficiency must be made through improved processes and catalysis. The hydrotreatment process could be made more energy efficient by using high lignin to solvent ratios, thereby reducing losses due to solvent heating and recovery. A solid acid could be used to replace the phosphoric acid, removing the need for recovery and reducing chemical waste. A mesoporous solid acid such as a zeolite could be used, allowing for the deposition of catalytic heteroatoms in the pores of the material. Pore sizes of 10 nm would allow good separation of unconverted lignin from breakdown products, but not so small as to restrict diffusion of the smaller molecules away from the raffinate (Wilson and Clark 2000.) The primary challenge to the use of solid acid catalysts as supports for the catalytic metal will be their instability in high temperature aqueous solutions.

As an unproven technology for the conversion of macromolecules, electrocatalytic hydrogenation would need significant process improvements to allow for the efficiencies assumed for the energy consumption calculated, Table 3. The development of electrolytic systems with low overpotentials using catalytic electrodes deposited directly on ion transport membranes and the development of continuous processing systems could dramatically improve the efficiency of current batch testing systems.

As mentioned earlier, the combination of hydrogen atoms on the surface of the cathode to produce hydrogen gas competes with the hydrogenation of lignin. Methods to improve the transport of reactants to the catalytic surface have been shown to significantly increase the hydrogen efficiency of electrocatalytic hydrogenation. Cirtiu et al. (2007) demonstrated that functionalized support surfaces with an affinity for reactant molecules can greatly improve the electron efficiency of electrocatalytic processes.

The development of a system capable of cracking ether linkages and deoxygenating lignin in one step

would allow for direct conversion of lignin to phenols. Unfortunately, performing heterogeneous catalytic reactions on solid macromolecules at low temperatures can be challenging due to diffusion limitations, steric hindrance, and poor access of the reactant molecules to catalytic sites, particularly in nano-porous materials (Wilson and Clark 2000, Thomas 1999).

A high temperature and pressure electrocatalytic hydrogenation system might be capable of depolymerizing and deoxygenating without the need for a separate hydrogen gas stream. The use of methanol as a co-solvent allows for the production of adsorbed hydrogen at a lower potential via the electrolysis of methanol to CO_2 and H_2 . Since polymer membranes degrade at high temperatures, solid acid proton transport membranes could be used with the anode and cathode deposited directly on opposite sides of the membrane as shown in Fig. 3. Sulfonated zirconium phosphate, for example, has been studied as a high temperature proton transport membrane for fuel cells. (Hogarth et al. 2005) Lignin dimers and oligomers could then be separated from the phenolic monomers using membrane filtration technology (e.g., Phelps et al. 2008).

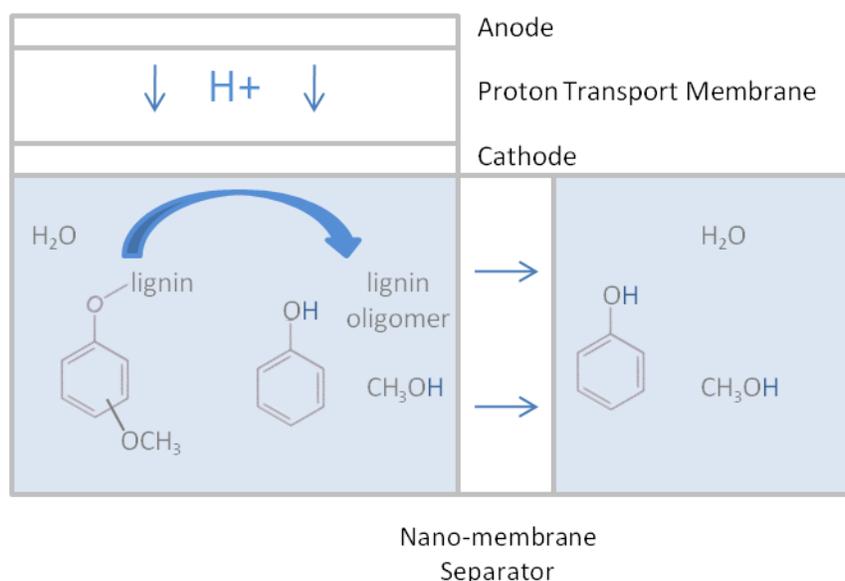


Fig. 3. Schematic of electrochemical cell for lignin conversion to phenolic compounds using a solid acid proton transport membrane.

Fig. 2 does not include cleavage of the C-C linkages between the aromatic groups in lignin, or repolymerized lignin conversion products. Development of a process to target C-C bonds would allow for the greatest improvement in the yield of mono-aromatic phenols. Unfortunately, the cracking of C-C linkages between aromatics is currently achievable only at high temperatures and pressures (Nishimura 2001).

2.3 HYDROTHERMAL ROUTE

Fast pyrolysis is a relatively new technology for converting whole biomass into complex liquid fuels (Kalita et al. 2009). The bio-oil, produced from fast pyrolysis in yields up to 75 wt%, is a free flowing, complex mixture of water, organic acids, aldehydes, ketones, sugars, phenolics, and lignin derived oligomers (pyrolytic lignin). (Ingram et al. 2008) Though bio-oil can be used as a low sulfur, carbon neutral fuel, its high viscosity, instability, poor miscibility with petroleum fuels, water content,

and hence corrosiveness, suggest that further treatment could significantly increase its fungibility and therefore, its value.

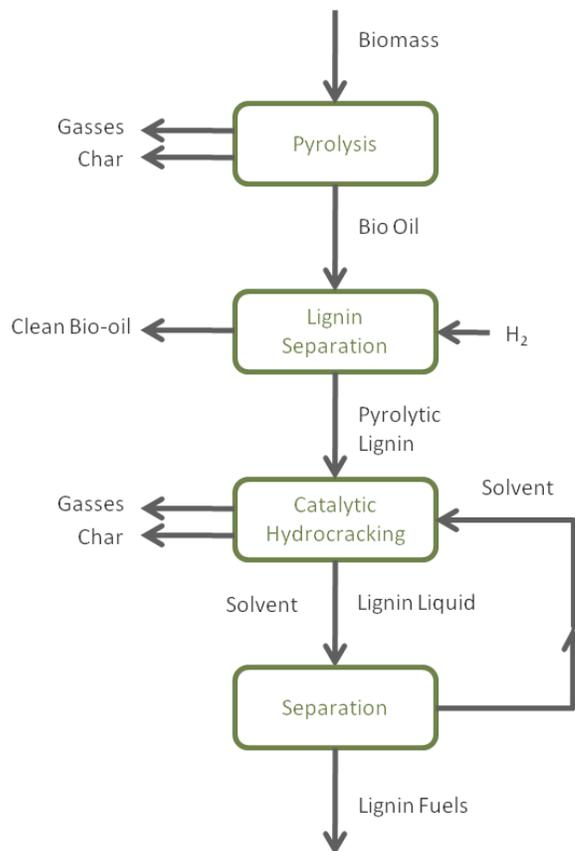


Fig. 4. Process overview for the conversion of pyrolytic lignin to mixed fuels.

The pathway proposed in Fig.4 involves the separation of pyrolytic lignin from bio-oil and its subsequent catalytic hydrotreatment to produce deoxygenated fuels. The treatment of raw bio-oil in this manner is analogous to the refinement of crude oil, where the lignin is analogous to heavy oil.

Pyrolysis processes have been extensively reviewed by Bridgwater et al. (1999) and Bridgwater and Peacocke (2000), the former paper describing the process, feedstock, and products and the latter providing detail on reactor configurations. Fast pyrolysis of whole biomass involves temperatures above 700K (Britt et al. 1999), often under anaerobic conditions at atmospheric pressure (Elliot 2007) or under moderate H_2 pressures up to 8-10 MPa. Residence times with flash pyrolysis are a few seconds or less, with quick quenching to prevent the formation of excess char or gaseous products (Serio et al. 1994).

Pyrolytic lignin increases the viscosity and reduces the chemical stability of bio-oil (Garcia-Perez et al. 2008). The lignin rich fraction of bio-oil, which constitutes roughly 25% of bio-oil's mass, can be separated by a variety of methods reviewed by Bridgwater and Peakcocke (2000), allowing for the subsequent upgrading of the pyrolytic lignin and bio-oil streams. It should be noted that the removal of pyrolytic lignin (24 –26MJ/kg) (Gayubo 2010) will reduce the already low heating value of bio-oil (16M–19MJ/kg). (Demirbas 2002) As such, the effect of pyrolytic lignin valorization on the overall energy balance of biomass fast pyrolysis should be assessed before choosing a pathway that looks

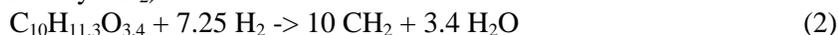
promising for lignin alone.

Bayerbach et al. (2009) have shown that pyrolytic lignin exhibits fewer methoxy moieties and more C-C bonds bridging aromatic groups than other manufactured lignins, suggesting that the structure of pyrolytic lignin is a result of both recombination reactions and ejection of intact lignin during and after fast pyrolysis. As such, processes used to convert pyrolytic lignin to phenolic monomers must focus on the cleavage of alkyl linkages, which are stronger than the ether linkages dominant in other technical lignins. As such, the valorization of pyrolytic lignin will likely require more sophisticated conversion technologies than those necessary for other technical lignins with more ether linkages.

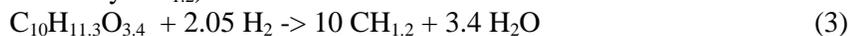
Pyrolytic lignin can be treated hydrothermally to produce deoxygenated aromatic or aliphatic compounds. Hydrothermal treatment, also termed oxy-organic hydrodeoxygenation or HDO, has been extensively reviewed by Bridgwater (1994) and Elliot (2007). HDO generally involves catalytically converting the reactants under high temperatures and high hydrogen gas pressures.

The amount of hydrogen required for hydrothermal treatment depends on the oxygen content of the lignin and the degree of saturation of each product stream, as indicated in Equations 2 and 3.

(production of naphtha, nominally CH₂)



(production of aromatics, nominally CH_{1.2})



2.3.1 Energy and Economic Analysis of Hydrothermal Route

Tang and colleagues (2010) reported a method to produce liquid fuels from pyrolytic lignin via catalytic hydrocracking in supercritical ethanol in a hydrogen atmosphere using Ru catalysts on SBA-15 mesoporous silica acidified with SO₄²⁻ and ZrO₂. The yield of liquid products from lignin was as high as 99.5% depending on catalyst preparation and the heating value of the fuel reached a maximum of 35 MJ/kg. Unfortunately, 11% – 13% of the ethanol used as a solvent reacted to form products in each run. Though Tang's process differs significantly from the solvent-less hydrotreatment that needs to be developed for the economical cracking of lignin, it is representative of the current state of lignin hydrotreatment technology. Improved processes as described by Yakovlev et al. (2009), with results given from their paper in Table 3, promise better product selectivity to phenols or further deoxygenation to long alkanes.

Table 3: GC detectable products from the hydrocracking of pyrolytic lignin

| Catalyst | Phenol | Anisole | Ketone | Acetal | Ester | Alcohol | Long Alkane | Poly-aromatic | Other |
|-------------|--------|---------|--------|--------|-------|---------|-------------|---------------|-------|
| No Catalyst | 38.22 | 3.35 | 0.82 | 0.08 | 7.43 | 0 | 14.30 | 12.57 | 2.40 |
| RuZr | 36.05 | 9.03 | 4.86 | 1.37 | 8.61 | 7.89 | 5.0 | 2.28 | 4.57 |

The energy consumption of the process was estimated by determining the work necessary to compress the hydrogen in addition to the heat required to increase the temperature of the lignin and catalyst mixture. Effects due to heat of reaction were ignored, likely providing a conservative estimate of the energy requirements. A molar ratio of 4 H₂ per lignin monomer and a weight ratio of

lignin to ethanol of 1:5 were assumed. This gave an energy consumption of 3.8MJ/kg lignin, assuming no heat recovery. It should be noted that 2.7MJ/kg goes toward the heating of the ethanol alone. Though the estimated energy consumption was low compared to the yield of high heating value products, Tang et al reported that an amount of ethanol equivalent to 50% of the mass of lignin would also be consumed in the supercritical process.

2.3.2 Hydrothermal Treatment of Heavy Oil

Differences between hydrodeoxygenation (HDO) of bio-oil and HDO of heavy crude are related to the composition of the feedstock. In bio-oil, the oxygen content is much higher, whereas heavy oil treatment requires more removal of nitrogen or sulfur. The oil shale crude is highly aromatic. Furimsky (2000) reports that the hydrogen to carbon ratio is 1.5 for oil-shale crude versus 2 for bio-oil. While hydrotreatment of heavy oil often involves sulfide catalysts that perform best under steady concentrations of sulfur, optimal catalysts will be different for biomass. Less sulfur content, at least in the case of Organosolv lignin, may allow the use of cheaper catalytic metals. Alternatively, noble metal catalysts may experience slower deactivation in low sulfur environments.

2.3.3 Suggested Process Improvements

Much of the research in hydrotreatment technology to date has been for use on fossil-based feedstocks, which can contain sulfur impurities. Biomass feedstocks like lignin will require research focused on the development of catalysts that can reduce oxygen content and cleave complex macromolecules while avoiding the formation of char or low-value gaseous byproducts. Typical catalysts for hydrothermal treatment include sulfided Co-Mo and Ni-Mo catalysts. The low sulfur content biomass suggests that non-sulfided catalysts for biomass HDO should be developed. Yakovlev and colleagues (2009) reported that successful catalysts for the treatment of biomass are bifunctional and often bimetallic catalysts composed of a transition metal oxide to activate oxygen groups and noble metals for the activation of hydrogen atoms from hydrogen gas. The Yakovlev group tested catalysts for hydrotreatment activity on the lignin model compound anisole with some success, but further testing needs to be performed on whole lignin.

Bryse and colleagues have published a review of support effects in hydrotreating catalysts (1991). They also describe their own work where they have tailored both the catalyst support and the catalytic metal particles to the requirements of biomass hydrodeoxygenation and hydrocracking to yield improved hydrothermal treatment. Changing the oxide support used from alumina to zirconia, resulted in a five-fold increase in the activity of a MoS₂ desulfurization and hydrogenation catalyst.

Though noble metals are the most effective catalysts for the activation of hydrogen gas, their high cost and potential for loss and deactivation in a catalytic cracking system suggest that cheaper catalysts should be used. Yakovlev (2009) reported the use of bimetallic nickel-copper catalysts with activities superior to monometallic nickel catalysts and comparable to noble metal catalysts for the hydrodeoxygenation of anisole. Hydrogen for the conversion of lignin could also be generated using a catalyst capable of performing the water-gas shift reaction on the gasses produced during conversion (Bridgwater 1994). Alloy nanocatalysts (10-20 nm NiB and CoB particles) have been demonstrated to have much higher activities and higher selectivities in hydrogenation than standard Raney nickel catalysts. The product distribution depended on the solvent used to synthesize the catalysts and the solvent used for the reaction, as well as the composition of the catalyst (Chen et al. 2005).

The use of circulating bed reactors could also increase the efficiency and selectivity of lignin valorization by allowing for the optimization of catalyst recovery and reaction in separate vessels. This would allow the use of more expensive engineered nanocatalysts that have demonstrated higher

selectivity and yields in hydrodeoxygenation processes.

2.4 LIGNIN PYROLYSIS

The Kraft process is the most common method to separate cellulose fibers from wood for the production of paper (Chakar and Ragauskas 2004). Black liquor, a byproduct of the Kraft process, contains the majority of the lignin and is normally concentrated and burned for process heat and power generation. Though heat and energy production from black liquor is currently well integrated in the pulp milling industry (Binder et al. 2009), the boilers used by much of the industry eventually need replacement because of chemical corrosion, increasing the likelihood that new technologies to convert Kraft lignin into fuels will be implemented (Consonni et al. 2009)

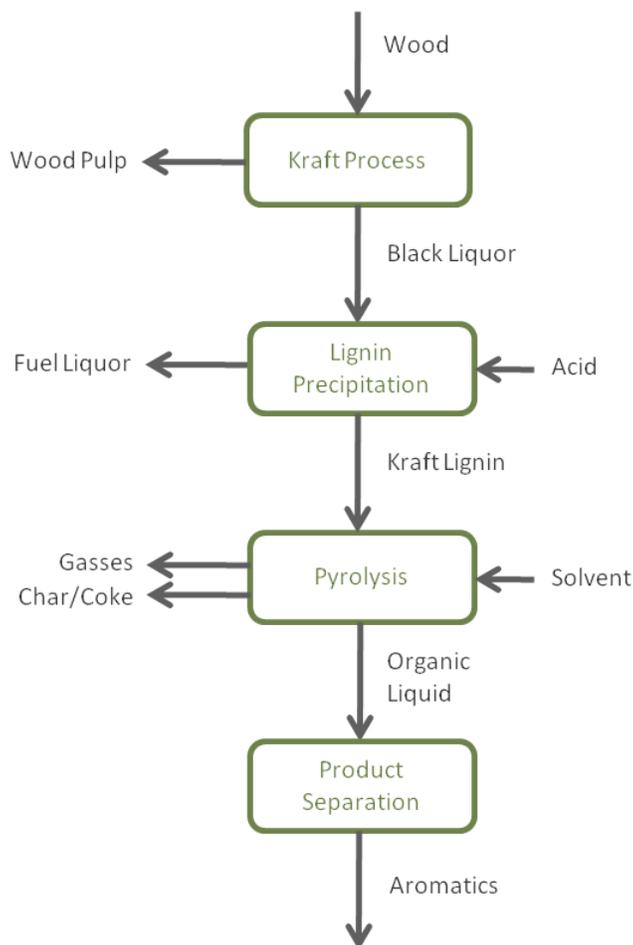


Fig. 5. Process overview for the conversion of kraft lignin to simple aromatics.

This process, Fig.5, involves the direct catalytic pyrolysis of purified Kraft lignin to produce phenols and deoxygenated aromatic liquids such as toluene and xylene. Though a desulfurization step may be necessary to prevent sulfur contamination of the final fuel additive, it will not be considered here. As paper mills currently produce black liquor as a process byproduct, it is only necessary to consider the inputs associated with the upgrading of the black liquor to fuels or chemicals against the current production of energy and heat when assessing the energy balance and economics of the process for implementation in the near future. Though the pyrolytic process proposed here is very similar to the

hydrothermal treatment discussed above, it should be kept in mind that pyrolysis is temperature driven while hydrothermal treatment is hydrogen potential driven.

The Kraft lignin contained in black liquor can be recovered by lowering the pH of the black liquor and filtering the resulting precipitate, leaving the remaining black liquor to be gasified for the production of heat and power. Kraft lignin contains sulfonate groups on the alkyl moieties, fewer ether linkages, and more C-C linkages between aromatic monomers than solvent extracted lignins, making it harder to process.

Due to the complexity of working with lignin, many detailed chemical studies have focused on the pyrolysis of chemicals that simulate the ether-cleaved breakdown products of lignin. For instance, Britt and colleagues (1999) found that the main products from pyrolyzed lignin simulant chemicals included: 56% phenol and 40% alkylated benzenes from phenethyl phenyl ether, 57% substituted phenols from phenethyl o-methoxyphenyl ether, and o-cresol (24%) and other substituted methoxy phenols from phenethyl 2,6-dimethoxyphenyl ether.

While uncatalyzed pyrolysis can be carried out, catalyst development has taken place to increase yields and selectivity of pyrolytic processes. Zeolites have been used in the conversion of larger organic molecules (e.g., Vermeiren and Gilson 2009), and as such they have been considered for use in biomass pyrolysis. Zeolites with subnanometer pore sizes and high silica to alumina ratios have been found to increase production of liquids and to minimize production of coke in biomass processing (Huber et al. 2009). Upgrading of pyrolysis vapors has also been carried out using zirconia/titania catalysts (Lu et al. 2010). Hydrogenation has also been carried out using Ru/C catalysts, giving oil yields of 65 wt.% after 4 h (Wildschut et al. 2010).

Though char and gasses are not the desired products of this process, they could be recovered to allow a kraft mill to continue producing some power and heat from its lignin waste stream.

2.4.1 Process Analysis

Energy consumption and valuable product yields for the process were assessed based on the products generated from the pyrolysis of Asian Lignin over HZSM-5 at a temperature of 600°C as reported by Jackson et al.(2009), Table 4. Their pyrolysis produced deoxygenated aromatic and naphthenic liquids with yields near 22 and 24 wt.%, respectively. Unfortunately, the process also produced 31 wt.% solid products on the zeolite catalysts. However, the bench scale process used by Jackson et al. does not recreate the pyrolysis conditions in an industrial reactor, as the heating rate and mass transport rates were much lower in his tests. As Asian lignin was used in the study, products and yields for Kraft lignin may be slightly different due to the impurities and more refractory bonds contained therein.

Table 4: Product yields as wt.% of total products

| Solids | | Liquids | | Gases | |
|---------------|----|----------------------------|------|-----------------|------|
| Char and Coke | 31 | Benzene | 4.0 | Methane | 1.0 |
| | | Toluene | 12.8 | Ethene | 1.0 |
| | | Xylenes | 6.8 | Ethane | 0.5 |
| | | Ethyl Benzene | 0.57 | H ₂ | 0.2 |
| | | C ₉ + Aromatics | 2.2 | CO | 10.4 |
| | | Unidentified | 3.3 | CO ₂ | 7.8 |
| Total Solids | 31 | Total Liquids | 47 | Total Gases | 22 |

The energy necessary for the pyrolysis of the solution was determined by calculating heats of reaction for the formation of products from lignin at room temperature and adding the energy necessary to heat those products to 600°C, Table 5. The heat of formation of a lignin monomer, which was used to calculate the heat of reaction of the pyrolysis of lignin, was calculated based on a heat of combustion for lignin of 25kJ/g and assuming that lignin can be represented by a $C_{10.2}H_{13.6}O_{3.2}$ monomer.

Table 5: Energy necessary for the pyrolysis of 1kg of lignin

| Lignin Pyrolysis Energy Consumption (kJ) | |
|---|-------|
| Energy for heating | 1100 |
| Energy for reactions | 4200 |
| Energy unit product (kJ/kg liquid) | 11300 |

This approach led to a total energy consumption of 5300kJ/kg lignin, though the heat requirements could be met by burning the gas or solid byproducts. Separation of the liquid and gaseous products would be necessary, though the energy consumption for separations was not considered. Efforts to improve the process could decrease energy use by lowering the pyrolysis temperature or improving the yield of liquid products.

2.4.2 Suggested Process Improvements

Kraft lignin was chosen for this study due to its availability, though it presents issues with impurities that other lignins may not have. For instance, Kraft lignin contains salts, extractives, sulfur, and H_2O – up to 10 wt% if there is significant carbohydrate content. Desalting during pretreatment could also remove low molecular weight compounds as organic salts, and changing the hydrophile-lipophile balance, thus affecting pyrolysis (Compere et al. 2005).

As the processing requirements for pyrolysis and hydrothermal treatment are similar aside from the lack of high hydrogen pressures in pyrolysis, both processes will face catalyst and char separation and recovery issues.

It is difficult to ensure contact between solid reactants and heterogeneous catalysts. When using a solid matrix and a solid catalyst, grinding or ball milling before introducing the mixture into the reactor could be beneficial by increasing both the interfacial contact between the powders and the number of reactive sites in the catalyst (Zhang et al. 2009).

Research on lignin pyrolysis processes should focus on improving the yield of deoxygenated liquids while reducing the formation of char. High process temperatures result in high conversion rates. Conversely, there is a need to keep temperatures below 350-400°C to minimize amount of char, which also deactivates the catalyst.

Reviews by Bridgwater and Peacocke (2000) suggest that a fluidized bed reactor gives the best efficiencies in pilot-scale implementations of pyrolysis. Shallow bubbling fluid beds, with residence times controlled by the fluidizing gas flow rate, may lead to even better process control (Huber et al. 2006).

In fast pyrolysis, the off gas and aerosols are passed through a cyclonic precipitator to remove

unwanted solid impurities and char. With the introduction of nanocatalysts, this separation could become more difficult, as these small particulates would likely remain entrained in the gas stream. Hence, securing of the catalyst to a support, or a secondary collection point for collecting the zeolite catalyst would need to be engineered, perhaps taking advantage of the charging of small particles. Larger liquid droplets are trapped according to size and volatility, and residual aerosol would be collected using an electrostatic precipitator. The liquid fractions would contain most of the fuel or aromatic building block precursors from the pyrolysis process, but possibly also some of nanocatalyst. Alternatively, the catalyst could be immobilized on an inert membrane, Fig. 6, as suggested by Phelps and colleagues (2008). Carbon molecular sieve substrates (Kiyono et al. 2010) as well as other inorganic supports should be inert and robust even under pyrolytic conditions.

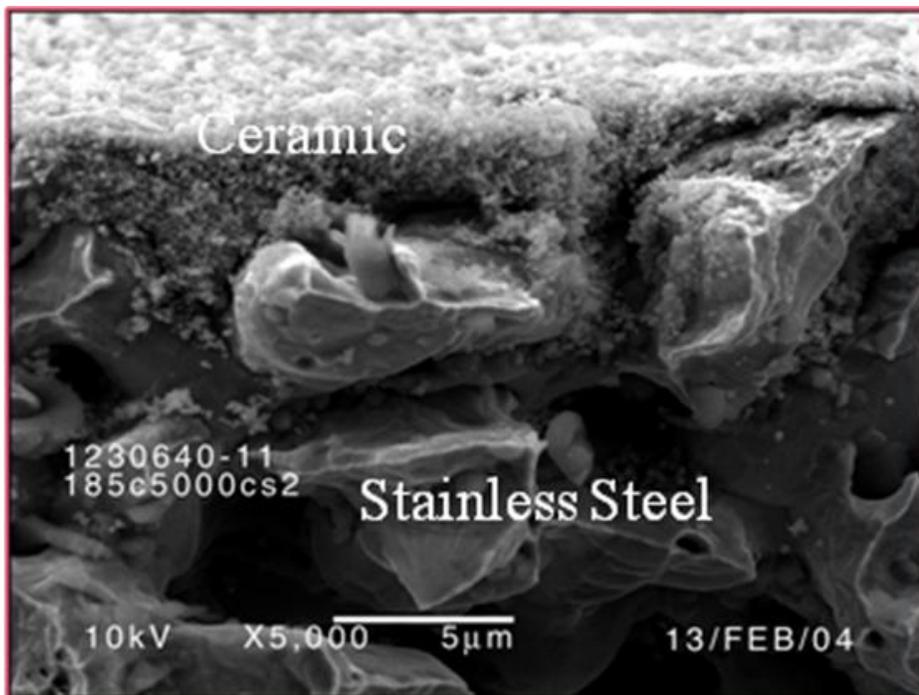


Fig. 6. Electron micrograph showing thin ceramic separative layer on metallic support.

3. EXPERIMENTAL

Various methods have been developed to breakdown lignin and so experiments were carried out to compare the effectiveness of these methods for converting lignin to smaller compounds. Three different experiments were tried: homogeneous reaction in BBR_3 , hydrogenation with an oxo-Rh catalyst, and electrocatalytic hydrogenation (ECH) of lignin in aqueous solution. Although the oxo-Rh catalyst has nanoscale dimensions, the process is considered a heterogeneous catalysis. The ECH method was tested with Pd and Ni catalysts loaded onto a carbon foam substrate. Deposited as oxidized salts, the metals were reduced *in situ*. This is the method that would most readily lend itself to a nanomanufacturing process.

3.1 MATERIALS

The experimental tests used simulated lignin compounds with appropriate ether linkages and oxygen containing groups. These included syringic acid (Alpha Aesar Lot #10097437), trans-cinnamic acid (Aldrich Lot #MKBB7111), 3,4-dimethylbenzoic acid (Alpha Aesar Lot#G13FA012657), 2,6-dimethoxybenzoic acid (Alfa Aesar Lot#J6276A) and phenylethylphenylether (Frinton Laboratories, Lot #FR-538). After these were tested, a synthetic lignin was used, Organosolv (Aldrich 06613MU), chosen for catalysis tests because it does not contain sulfur.

3.5 ANALYSIS

Mass balance results were derived from gravimetric data.

Speciation data were collected using an Agilent 6890 Gas Chromatograph Mass Spectrometer (GC MS), and quantitative gas chromatographic data were collected on a Hewlett Packard (HP) 5890 Flame Ionization Detector (FID). Both GCs were run with DB5 columns. Tribromophenol (Aldrich Lot#18324MR) or 4-ethyl resorcinol (Aldrich 07/28/1998) were used as recovery standards and naphthalene-*d*8 (Sigma Lot#55H36930) was the internal standard. The GC method followed: holding the inlet at 250°C, the detector at 340°C, setting initial temperature at 45°C for 3 min, having a ramp of 12 °C/min to 100°C, 4°C/min to 280°C, and having a final hold for 20 min. The injection was splitless because sample concentrations were so low. Samples were derivatized using BSTFA (Supelco Lot LB4190), or acetic anhydride (Aldrich JQ04920TN) with pyridine catalyst (Aldrich Lot#12513BN).

UV Spectroscopy was also undertaken on some of the samples, using a Cary 5000 UV-VIS-NIR Spectrophotometer.

The preparation of sample for GC analysis was quite involved because of the numerous fractions collected. A schematic of the analysis is given in Fig. 7.

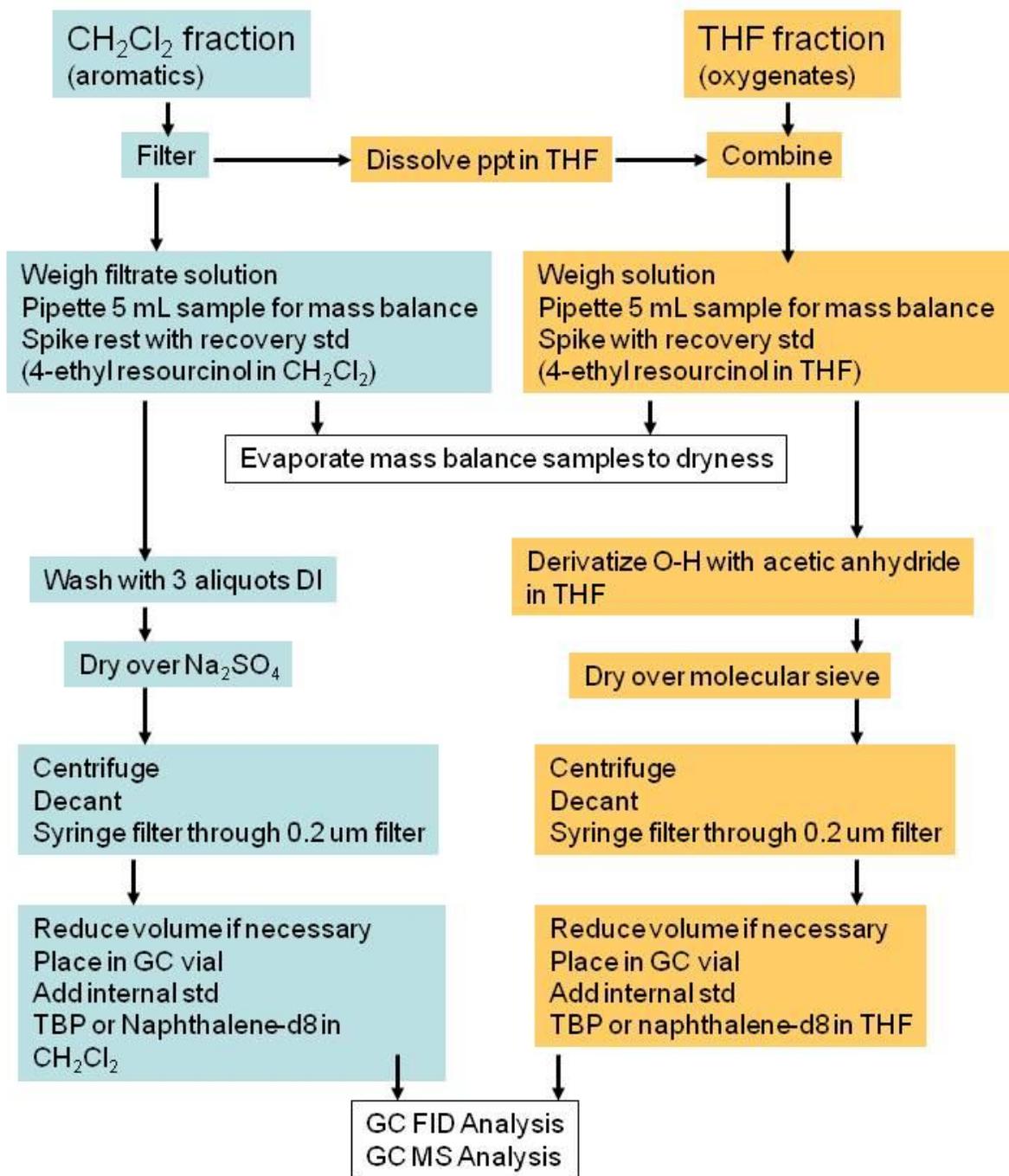


Fig. 7. Sample Analysis Flowsheet

3.3 BORON TRIBROMIDE TREATMENT

0.25 g of lignin was dissolved in 30 ml of CH_2Cl_2 (EMD Lot#49288) in a sealed round bottom flask. 1.0 ml of boron tribromide (Sigma Aldrich 03/23/2009) was introduced and the solution was allowed to react for 24 h under stirring. Prior to neutralization, naphthalene-*d*8 was added as a recovery standard. The reaction was neutralized with 5.0 ml water and the resulting neutralized solution and precipitate were filtered. The filtrand was rinsed with 5 ml deionized water and 5 ml dichloromethane. This process was very, very slow. The aqueous and organic phases of the filtrate were separated and the aqueous phase was extracted twice more with dichloromethane. The dichloromethane fraction was evaporated to about 1 mL and the resulting concentrated solution was qualitatively analyzed by GC-MS and quantitatively analyzed by GC-FID.

3.4 RHODIUM CATALYST TREATMENT

$\text{Rh}_6(\mu_3\text{-O})_4(\text{OH})_{12}$ was prepared from hexadecacarbonyl hexarhodium (Alpha Aesar 06/18/2009) using the process described in a paper by James, Wang, and Hu (1996). 0.200 g of organosolv lignin was dissolved in a mixture of 5 ml water and 5 ml ethanol. In other tests, 0.5 g of organosolv lignin acetate was sonicated for 1 h in 20 ml of 1:1 water:ethanol to yield a heterogeneous mixture. The rhodium catalyst was added to the solution and the mixture was placed in a stoppered vial. Hydrogen from a Packard hydrogen generator was slowly bubbled through the solution for 3-5 days. The excess hydrogen gas was bubbled through dodecane in order to collect any volatile organics produced during hydrogenation. The solution was evaporated to dryness and the resulting solid was dissolved in 2-methoxy ethanol. The solution was qualitatively analyzed by GC-MS and quantitatively analyzed by GC-FID.

3.5 ELECTROCATALYTIC HYDROGENATION

An electrocatalytic hydrogenation experimental apparatus was built based on the setup described by Cyr and Chiltz (2000), Fig.8. A catalytic cathode ($1.5 \times 1.0 \text{ cm}^2$ or 0.6 cm^3) was cut from reticulated vitreous carbon foam, 100 pores per square inch (ERG aerospace), and rinsed in deionized water and methanol to remove dust and loose carbon particles generated during cutting. The electrodes were then dried and massed. Catalytic metal was deposited onto the carbon electrode surface using incipient wetness impregnation of palladium. Palladium acetate (Sigma Lot#92H3431) or nickel nitrate hexahydrate (Aldrich Lot#09119ES) was dissolved in acetone (Burdick and Johnson Lot#DB247) and methanol (VWR Lot#7340) and the solution was pipetted onto the electrode. The concentration of metal salt was determined by measuring the amount of liquid absorbed per unit mass of carbon foam and adding the amount of salt necessary for a 5 wt.% loading of the catalytic metal. The electrodes were air dried at room temperature before being heated to 150-180°C. The palladium was reduced at 320-340°C under hydrogen for 1 h. A scanning electron microscope image of the loaded carbon foam electrode is given in Fig. 9, with X-ray photoelectron spectroscopy results given in Fig. 10. The morphology of the heterogeneous catalysts in these experiments is much larger than nanoscale; however, these preliminary tests allow a proof-of-principle approach to the investigation of the effectiveness of electrocatalytic hydrogenation.

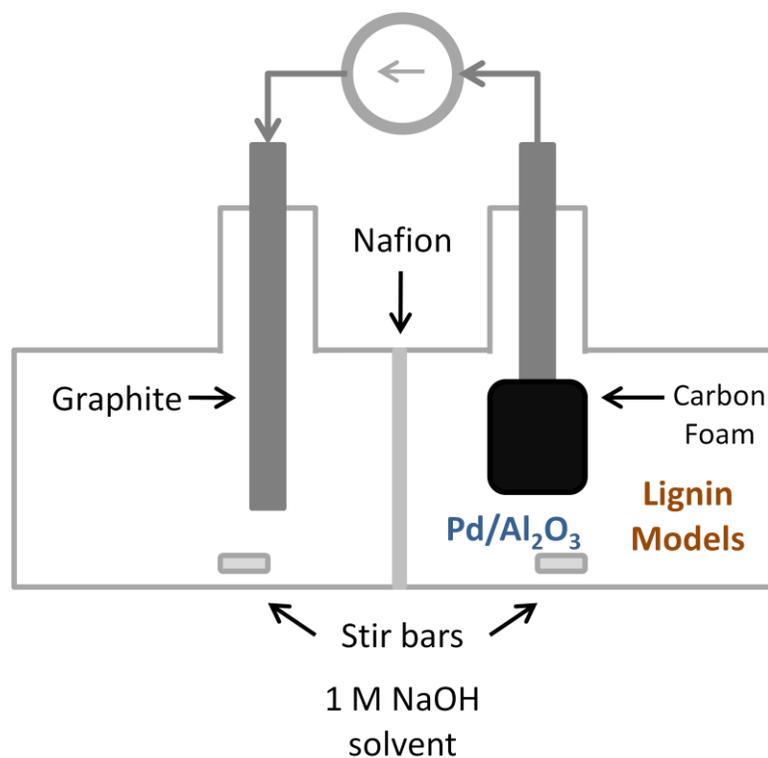


Fig. 8. Schematic of electrocatalytic hydrogenation apparatus.

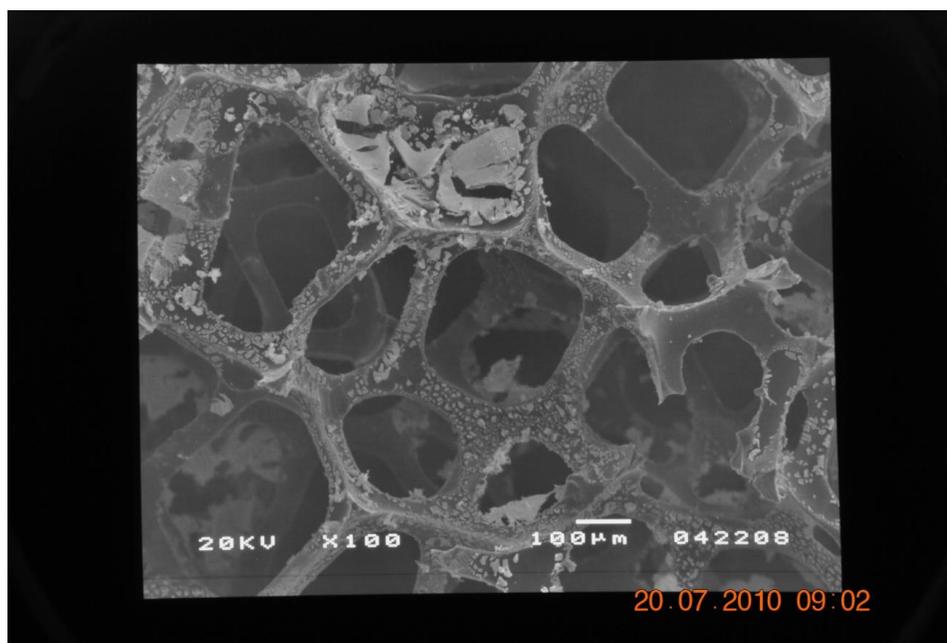


Fig. 9. Palladium catalyst deposited on carbon foam electrode before use in electrocatalytic cell. The picture shows the wide range of catalyst sizes present, from less than 1 micron to deposits over a 100 micron in diameter. The porosity of the foam electrode is also apparent.

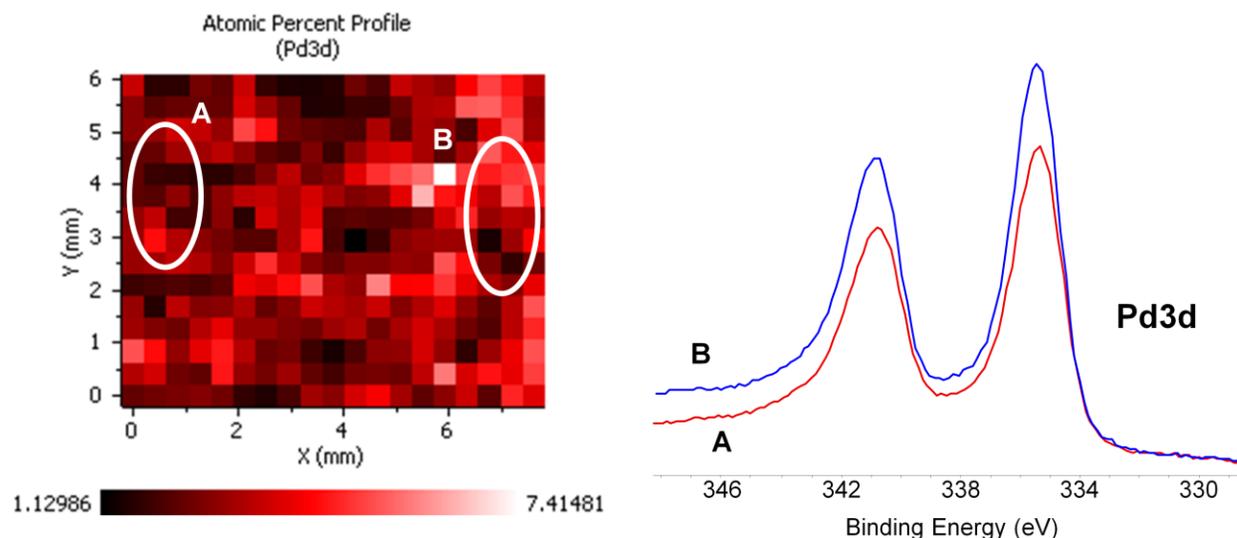


Fig. 10. X-ray photoelectron spectroscopy results for the carbon foam electrode pictured in Fig. 4. Analysis shows the Pd ranges from ~1 at.% to ~7at.% across the field of view of the spectrometer. The Pd binding energy shows that it exists primarily as a metal, given its lineshape and binding energy position.

Either a platinum wire or a 3.0 x 1.5 cm² piece of reticulated vitreous carbon foam was used as the anode. The catalytic electrodes were massed to determine loading and attached to graphite rods using carbon paint.

Two 100 ml compartments separated by a Nafion membrane were filled with 1 M sodium hydroxide (VWR Lot#8210), or with a solution of 5mM Na₂SO₄ (JT Baker Lot#3891-01) in 1:1 methanol and water by volume. Both compartments were stirred using stir bars. Both electrodes were held in inverted syringes in order to measure the volume of hydrogen and oxygen produced during electrolysis. Electrocatalytic hydrogenation was performed on solutions of organosolv lignin and syringic acid, a lignin model monomer. Prior to the addition of reactant (0.250g of organosolv lignin or syringic acid) to the cathodic solution, the electrocatalytic hydrogenation system was heated to 50-70 °C using heating tape and allowed to run at a constant voltage of 3 V for 1 hour in order to allow any oxidized metal to be reduced. After the addition of substrate, the system was run under a constant current of 7 mA and the voltage and gas volume were measured.

The catholyte and anolyte were removed from the cell and analyzed separately. Samples were analyzed by adding tribromophenol as a recovery standard. If used, methanol was removed from each solution using a rotovaporator. Analysis was carried out in two ways:

- either by acidifying the solution to pH 2 using hydrochloric acid (JT Baker Lot#5618-02), and derivatizing the compounds overnight using a mixture of pyridine and acetic anhydride. Extractions were performed using CH₂Cl₂ and the resulting extractions were analyzed by GC-MS and GC-FID with naphthalene d₈ as an internal standard.
- or a 2 mL sample of the aqueous solution was passed through a lichrolut EN solid phase extraction column and eluted with methanol.

The resulting solutions were qualitatively analyzed by GC-MS and the peaks were quantified using GC-FID. Quantitative analyses were performed in triplicate.

4. RESULTS

Before treatment, lignin compounds were analyzed by the GC MS to identify peaks associated with the untreated material. Peaks that appeared included mostly aryl esters (dimethylphthalate, diethylphthalate, bis-2-ethylhexyl apidate, diisooctylphthalate, isopropyl palmitate, 1,1-diethylmethylhexadecanoic acid, butyl stearate, mono-2-ethylhexyl phthalate), as well as a couple of large branched olefins (squalene and 2,6,10,14,18-pentamethyl-2,6,10,14,18-pentaene, C₂₅H₄₂).

4.1 BORON TRIBROMIDE ACIDOLYSIS

Gravimetric data were collected to assess the amount of lignin in each of the separated fractions, Table 6.

Table 6: Recovery of lignin and products in separated fractions after acidolysis

| Separated Fractions | Blank | BBr ₃ |
|---------------------------------|-------|------------------|
| Aqueous | 4% | ~15% |
| CH ₂ Cl ₂ | 53% | 6.3% |
| Undissolved | 30% | ~56% |
| Total | 87% | 77% |

GC-MS data combined with gravimetry showed that dibromocyclohexane and bromocyclohexane were produced in 0.74% and 0.49% yields, respectively. No other low molecular weight compounds that were not present in an unreacted solution of lignin were observed. Most of the lignin went into the filter cake. A better neutralization technique may avoid the formation of a recalcitrant solid. It should also be noted that the monomeric components of lignin form many peaks, hiding possible low molecular weight products.

4.2 HOMOGENEOUS HYDROGENATION

The GC MS showed substituted benzenes, naphthalenes, and polyaromatic hydrocarbons being formed (e.g. diphenylpropane, diphenylbutadiene, bismethylannulene, diphenylbutadiene, methylbutynlbenzene, and terphenyl compounds), which were not present in the original lignin. Fragments, such as 2-benzyloxy-1,2,-diacetyl-1,2-propanediol, were observed, as well as naphthenes such as 1,2-cyclohexanedicarboxylic acid – 1,2 bis(2-ethylhexyl ester). Although a mass balance was not possible because of the small quantities of material, the peaks attributed to the fragments were a factor of 16 greater in area than the phthalate peaks attributed to unreacted material. This suggested that the fraction extracted into CH₂Cl₂ included more converted than unreacted material.

In addition, the solubility of the lignin in an ethanol and water solvent was reduced, also suggesting production of insoluble hydrocarbons, possibly higher molecular weight polyaromatic materials. It is possible that this catalyst is not ideal for the conversion of lignin to deoxygenated aromatics as the

results from the paper from which this catalyst was taken suggest that the catalyst hydrogenates the aromatic ring but does not break down the lignin. This, however, was not observed in these experiments.

4.3 ELECTROCATALYTIC HYDROGENATION

Gas volumes from ECH for the syringic acid and lignin samples are given in Figs. 11 and 12, respectively. The gas volume produced from the electrolysis of water was measured to be only slightly lower than the theoretical value in both cases. The observed differences could have arisen from consumption of hydrogen in the reaction to convert syringic acid or lignin respectively. From the figures, the amount of hydrogen consumed was very low. Hence, the rate of production did not limit the amount of hydrogenation in either chemical system.

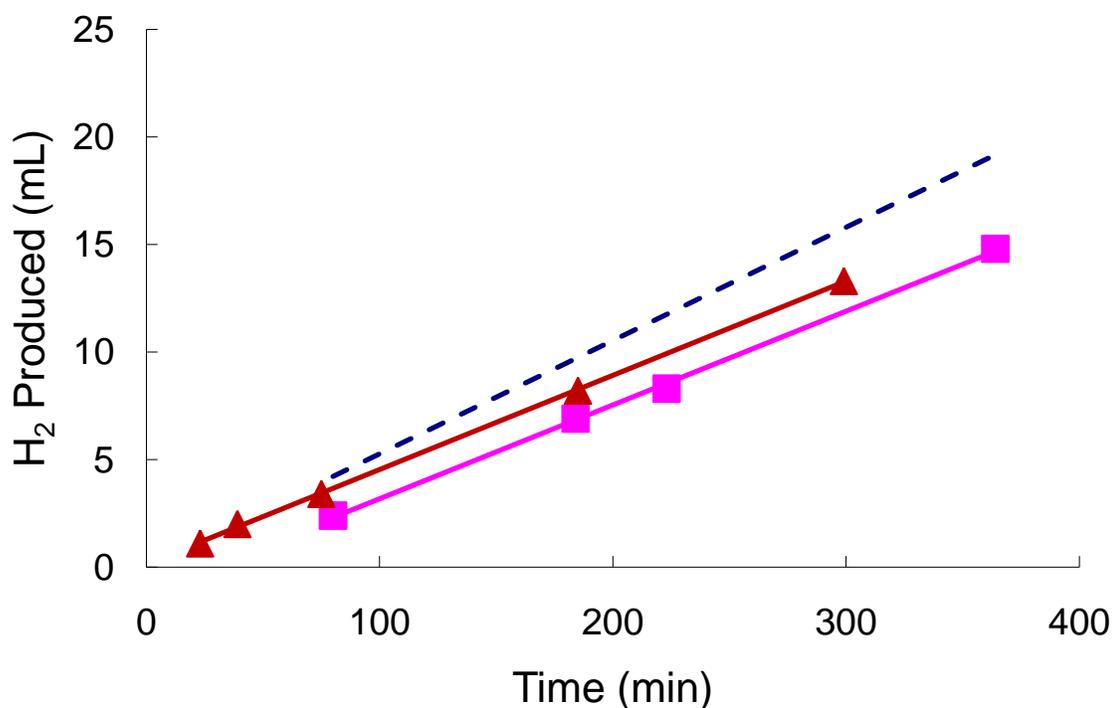


Fig. 11. Production of hydrogen during ECH of syringic acid. Theoretical values are dashed. Data are shown from 2 separate experiments.

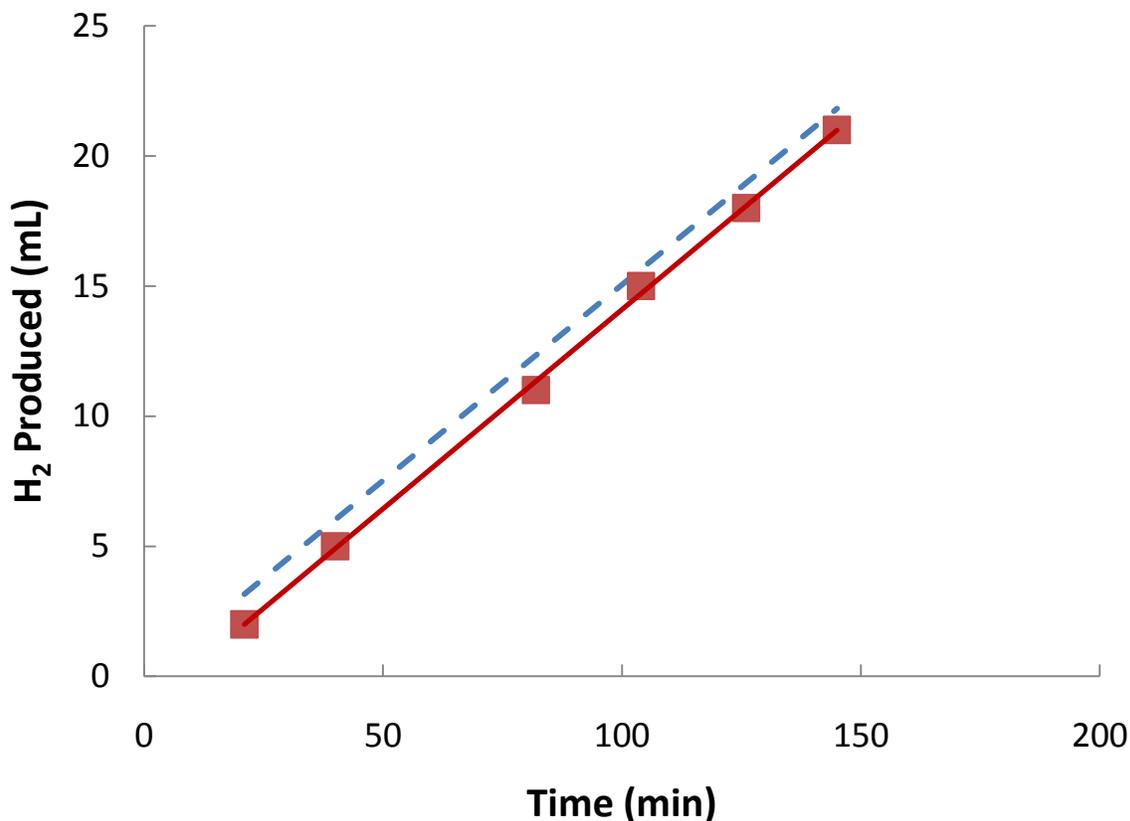


Fig 12. Hydrogen production from the ECH of lignin. Theoretical values are shown as a dashed line.

The ECH of phenylethylphenylether was carried out and results from UV Spectroscopy are shown in Fig. 13. The sample was highly UV absorbent, so very diluted samples were examined. Possible breakdown products are shown on the same chart for purposes of comparison: lignin monomers such as cinnamic acid having absorptions at 280 nm, small aromatics below 280 nm, with linked aromatics above 300 nm, and linked phenols 260-280 nm. The absorption spectroscopy suggests that the decomposition products from phenylethylphenylether have spectra that best overlap with that of small aromatic molecules, such as toluene. Heterocyclic products, phenols, and cross-linked polyaromatics are not seen.

The GC MS results for ECH treated versus untreated lignin are quite different. The untreated lignin shows several diethylphthalate peaks that are minor components of the treated sample. The ECH results show a series of peaks corresponding to long-chain paraffins: from eicosane, C₂₀H₄₂, through to tetracosane, C₂₀H₅₀. These peaks were at very low yield; however, and could have arisen from contamination on the column.

Unlike published experiments for ECH of simulant compounds, the ECH of lignin itself has very poor yield. Further testing is needed before it is known if the issue relates to the physical properties of the lignin, chemical kinetics and steric effects, or to transport of lignin in the catholyte to the electrode.

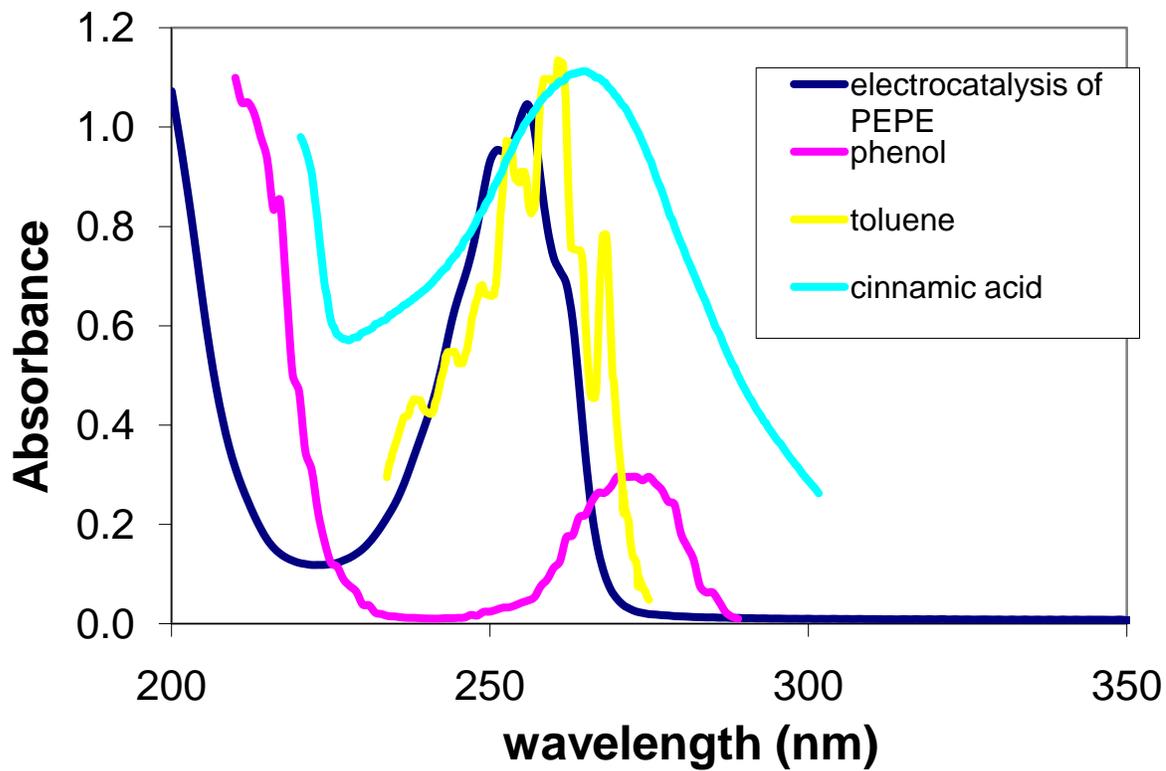


Fig. 13. UV absorption of the ECH products of phenylethylphenylether (PEPE). Also shown are the spectra of possible conversion products for comparison.

5. NANOMANUFACTURING IN LIGNIN CONVERSION TO FUELS

5.1 PRODUCTION

The catalysts considered in this report use materials that are typically used in industrial processes. Noble metals are used in vehicle emissions catalysts, jewellery, electronics, and dentistry. Although North America has some reserves, the main source of these metals is overseas, primarily from South Africa and Russia (Kendall 2004). Hence, any processes that rely on these metals are also susceptible to difficulties in supply security. Not all of the metals have the same price structure, however. The price of platinum has risen steadily over the last decade because of the perception of insufficient supply to meet demand, while the prices of the other precious metals, Pd and Rh, have dropped.

Costs and security issues associated with production could be mitigated by developing better ways to capture and recycle precious metals from waste streams. Currently, the largest recycling industry associated with these metals is associated with the auto catalytic converters. However, only 10% of the platinum used in the automobile industry comes from recycled material. In developing large scale processes for chemicals production, source of catalyst, including recycled material, would have to be a key element of the research into feasibility.

5.2 USE

In bench-scale experimental studies, the mass ratio of catalyst to lignin can be quite large, for instance 3:1 in the gasification of lignin reported by Osada et al. (2003). In the experiments reported here, similarly large amounts of catalyst were used to push the kinetics of the process to completion. If large amounts of lignin are to be converted, however, high surface area catalysts must be made to have good contact with lignin and its products without being poisoned. This is one of the most compelling arguments for the use of supported nanocatalysts in lignin decomposition. In developing these technologies, investigation of regeneration of catalyst should also be considered. Ideally, the catalyst will be strongly attached to the supporting material, so that losses during use and regeneration are minimal. Nanoscale catalysts may also be agglomerated to make larger particles, for instance through electrocoagulation, that can be more easily trapped in filters before release to the environment (Den 2006). Research activities are needed to investigate sensors for catalyst transport and potential losses in all process streams, so that major loss avenues can be identified, targeted and mitigated.

5.3 FATE

Inevitably, with such large volumes of process material, catalysts will be released into the environment. This has been observed with radioactive platinum and palladium tracers released in small amounts in vehicle exhaust (Hill and Mayer, 1977). Because of the complex chemistry of lignin, multiple separation steps will be needed, and in any of these, catalyst loss is a possibility. These loss mechanisms and possible release to the environment must be identified. Chemical speciation will affect the partitioning of nanomaterials in the atmosphere, soils, and water. For instance, iron oxide associated with carbon may behave similarly to wood flyash (Kastner et al. 2008). Finally, toxicology studies need to be carried out to ascertain the risk of using nanocatalysts containing bound transition metals to the nearby populations and to the local ecology (e.g., Bérubé et al. 2007).

-

6. CONCLUSIONS

Lignin has the potential to be an abundant source of organic aromatic chemicals for fuels and polymer production; one that is not currently being utilized to its full potential. Issues with lignin usage come from its variability. Its chemical composition changes with the source plant, the environmental conditions, pretreatment, and separation during initial processing to remove the cellulose and hemicelluloses. The objective of this project was to highlight areas that hamper the thermochemical conversion of lignin, with an emphasis on relatively low temperature processes. This is the arena where catalysis in general, and nanocatalysis in particular, may play the greatest role in permitting lignin conversion to become feasible on an industrial scale and have a real impact on the energy security of the US.

The analysis reported here has attempted to investigate three very different feedstocks and processes for the production of fuels and aromatic chemicals from lignin. Of the three chosen, hydrotreating is the closest to commercialization, taking advantage of the catalyst research that has been used to break down heavy oil. Pyrolysis lignin is similar to heavy oil in that it has a relatively low oxygen content. For this technology to progress, however, catalysts specific to the decomposition of lignin need to be developed. For instance, catalysts that do not require addition of sulfur to the reaction would last longer, and would allow further processing to take advantage of the sulfur-free nature of the feedstock.

Flash pyrolysis has also been deployed in small scale commercial settings, although the scale is not comparable to conversion of lignin generated from a pulp and paper plant. As suggested in the text above, pulp lignin poses special challenges to large scale pyrolysis: pretreatment to remove impurities, sulfur content, and the need to design processes and catalyst beds that facilitate mass transfer on large volumes of material. Catalysts need to be inexpensive, robust, and either fixed or easily separable. Fairly successful studies have been carried out at bench-scale level, but scale up of catalyst beds to handle many tons of material is needed.

Electrocatalytic hydrogenation on organosolv lignin is the technology that is the furthest from commercialization, but has the most promise for specificity and on-line separation. Because conditions are mild, this the one step process to produce chemicals may be the best candidate for lignin processing based on advanced nanocatalytic substrates and materials. The technology has been demonstrated on model compounds, but has not yet been shown as effective for a macromolecule such as lignin. Hence this is an area of promise that needs much more research, from fundamental electrochemical studies, mounted metallic nanocatalytic materials, physical properties of lignin, intermediates and products to understand issues around solubility, and investigation of mass transport through the cell and control of the rate of reaction.

The nanocatalysts considered in this review are already used in large scale commercialization especially those used in the petroleum industry. The hydrogenation of phenol to cyclohexanone is an industrial process. The issues regarding implementation of nanocatalyst technology are akin to finding similarities between known and proven industrial processes and the conversion of lignin to fuels. A specific focus is needed on the effect of chemical differences between lignin, heavy oil, and sweet crude and how these would influence catalyst pathways. In addition, the source and fate of nanocatalyst in all steps of the process for lignin conversion must be considered in further analyses and research activities, as these will comprise much of the feasibility of the nanomanufacturing-based process.

7. REFERENCES

- Barth, T. 1999. "Similarities and differences in hydrous pyrolysis of biomass and source rocks", *Organic Geochemistry* 30, 1495-1507.
- Bayerbach, R. and D. Meier. 2009. "Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin). Part IV: Structure elucidation of oligomeric molecules", *J. Anal. Appl. Pyrolysis* 85(1-2), 98-107.
- Bérubé, K., Balharry, D., Sexton, K., Koshy, L., and T. Jones. 2007. "Combustion-derived nanoparticles: Mechanisms of pulmonary toxicity", *Clinical and Experimental Pharmacology and Physiology*, 34(10), 1044-1050.
- Beste, A. and A.C. Buchanan. 2009. "Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effects in phenethyl phenyl ethers", *J. Organic Chemistry* 74, 2837-2841.
- Binder, J.B., Gray, M.J., White, J.F., Zhang, Z.C., and J.E. Holladay. 2009. "Reactions of lignin model compounds in ionic liquids", *Biomass and Bioenergy* 23(9), 1122-1130.
- Botto, R.E. 1987. "Solid ¹³C NMR tracer studies to probe coalification", *Energy and Fuels*, 1(2), 228-230.
- Breyse, M., Portefaix, J.L., and M. Vrinat. 1991. "Support effects on hydrotreating catalysts", *Catalysis Today* 10, 489-505.
- Bridgwater, A.V. 1994. "Catalysis in thermal biomass conversion", *Applied Catalysis A: General* 116, 5-47.
- Bridgwater, A.V., and G.V.C. Peakcocke. 2000. "Fast Pyrolysis Processes for Biomass", *Renewable Sustainable Energy Rev*, 4, 1-73.
- Bridgwater, A.V., Meier, D., and D. Radlein. 1999. "An overview of fast pyrolysis of biomass". *Organic Geochemistry*, 30, 1479.
- Britt, P.F., Buchanan, A.C. III, and D.R. Martineau. 1999. "Flash vacuum pyrolysis of lignin model compounds: Reaction pathways of aromatic methoxy groups", *ORNL/CP-101275*.
- Buchanan, A.C. III, Britt, P.F., and J.A. Strus. 1997. "Investigation of reaction pathways involved in lignin maturation", *Energy and Fuels*, 11(1), 247-248.
- Chakar, F.S., and A.J. Ragauskas. 2004. "Review of current and future softwood kraft lignin process chemistry", *Industrial Crops and Products* 20(2), 131-141.
- Chen, Y.-Z., Liaw, B.-J., and S.-J. Chiang. 2005. "Selective hydrogenation of citral over amorphous NiB and CoB nano-catalysts", *Appl. Cat. A: General* 284, 97-104.
- Chiang, V.L. 2002. "From rags to riches", *Nature Biotechnology* 20, 557-558.
- Cirtiu, C.M., Brisach-Wittmeyer, A., and H. Ménard. 2007. "Electrolysis over Pd catalysts: A very efficient alternative to catalytic hydrogenation of cyclohexanone", *J. Catalysis* 245, 191-197.
- Compere, A.L., Griffith, W.L., Leitten, C.F., Jr., and J.M. Pickel. 2005. "Evaluation of lignin from alkaline-pulped hardwood black liquor", *ORNL/TM-2005/88*.
- Consomi, S., Katofsky, R.E., and E.D. Larson. 2009. "A gasification-based biorefinery for the pulp and paper industry", *Chem. Eng. Res. Des.* 87, 1293-1317.
- Cyr, A., Chiltz, F., Jeanson, P., Martel, A., Brossard, L., Lessard, J., and H. Ménard. 2000. "Electrocatalytic hydrogenation of lignin models at Raney nickel and palladium-based electrodes", *Can. J. Chem.* 78, 307-315.
- Demirbas, A. 2002. "Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels", *Energy Exploration and Exploitation* 20(1), 105-111.
- Den, W. 2006. "Mechanistic study of the continuous flow electrocoagulation of silica nanoparticles from polishing wastewater", *Ind. Eng. Chem. Res.* 45(10), 3644-3651.
- Deville, J.T., and V. Behar. 2001. "Chelation-controlled selectivity in the clay-catalyzed deprotection of phenolic methoxy methyl ethers", *J. Org. Chem.* 66911, 4097-4098.
- Elliot, D.C. 2007. "Historical Developments in Hydroprocessing Bio-oils", *Energy and Fuels*

21, 1792-1815.

Furimsky, E. 2000. "Catalytic Hydrodeoxygenation". *Applied Catal. A: Gen.* 199, 147-190.

Garcia-Perez, M., Wang, X.S., Shen, J., Rhodes, M.J., Tian, F., Lee, W.-J., Wu, H., and C.-Z. Li. 2008. "Fast pyrolysis of oil mallee woody biomass: Effect of temperature on the yield and quality of pyrolysis products", *Ind. Eng. Chem. Res.* 47, 1846-1854.

Gayubo, A.G., Valle, B., Aguayo, A.T., Olazar, M., and J. Bilbao. 2010. "Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation", *J. Chem. Technol. and Biotechnol.* 85(10), 132-144.

Graham, R.G., Freel, B.A., Huffman, D.R., and M.A. Bergougnou. 1994. "Commercial-scale rapid thermal processing of biomass", *Biomass and Bioenergy* 7, 251-258.

Guey-Lee, L. 2009. "Renewable energy consumption for nonelectric use by energy use sector and energy source", The US Energy Information Administration, April 2009. Downloaded on Aug. 10, 2010 from <http://www.eia.doe.gov/cneaf/solar.renewables/page/trends/rentrends.html>.

Hill, R.F., and W.J. Mayer. 1977. "Radiometric determination of platinum and palladium attrition from automotive catalysts", *Nuclear Science IEEE Transactions*, 24(6), 2549-2554.

Hogarth, W.H.J., de Costa, J.C.D., Dennnan, J., and G.Q. Lu. 2005. "Proton conductivity of Mesoporous sol-gel zirconium phosphates for fuel cell applications", *J. Mater Chem* 15(7), 754-758.

Huber, G.W., Cheng, Y.-T., Carlson, T., Vispute, T., Jae, J., and G. Tompsett. 2009. "Catalytic pyrolysis of solid biomass and related biofuels, aromatic, and olefin compounds", US Patent WO200911026.

Huber, G.W., Iborra, S., and A. Corma. 2006. "Synthesis of transportation fuels from biomass : Chemistry, catalysts, and engineering", *Chem. Rev.* 106, 4044-4098.

Ingram, L., Mohan, D., Bricka, M., Steele, P., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., C.U. Pittman, Jr. 2008. "Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils", *Energy and Fuels* 22, 614-625.

James, B.R., Wang, Y., and T.Q. Hu. 1996. "Hydrogenation of substituted aromatics", *Catalysis of Organic Reactions, Chemical Industries* 68, 423-428.

Jackson, M.A., Compton, D.L., and A.A. Boateng. 2009. "Screening heterogeneous catalysts for the pyrolysis of lignin", *J. Anal. Appl. Pyrolysis* 85, 226-230.

Kalita, P., Mohan, G., Kumar, G.P., and P. Mahanta. 2009. "Determination and comparison of kinetic parameters of low density biomass fuels", *J. Renewable and Sustainable Energy* 1(2), 023109.

Katagi, T. 1992. "Photodegradation of 3-phenoxybenzoic acid in water and on solid surfaces", *J. Agricultural and Food Chemistry*, 40(7), 1269-1274.

Katagi, T. 1991. "Photodegradation of the pyrethroid insecticide esfenvalerate on soil, clay minerals, and humic acid surfaces", *J. Agricultural and Food Chemistry* 29(7), 1351-1356.

Kastner, J.R., Ganagavaram, R., Kolar, R., Teja, A., and C. Xu. 2008. "Catalytic ozonation of propanal using wood flyash and metal oxide nanoparticle impregnated carbon", *Environ. Sci. Technol.* 42(2), 556-562.

Kendall, T. 2004. "Platinum 2004", Johnson Matthey.

Kiyono, M., Williams, P.J., and W.J. Koros. 2010. "Effect of pyrolysis atmosphere on separation performance of carbon sieve membranes", *J. Membrane Sci.* 359, 2-10.

Kleinert, M., and T. Barth. 2008. "Towards a lignincellulosic biorefinery : direct one-step conversion of lignin to hydrogen-enriched biofuel", *Energy and Fuels* 22, 1371-1379.

Knifton, J.F. 1998. "1998 Paul N. Rylander plenary lecture. New applications for inorganic solid acid catalysis", *Chemical Industries*, 75 (*Catalysis of Organic Reactions*), 1-11.

Lapierre, C., Pollet, B., Petit-Conil, M., Toval, G., Romero, J., Pilate, G., Leplé, J.-C., Boerjan, W., Ferret, V., De Nadai, V., and L. Jouanin. 1999. "Structural alterations of lignins in transgenic poplars with depressed cinnamyl alcohol dehydrogenase or caffeic acid O-methyltransferase activity have an opposite impact on the efficiency of industrial Kraft pulping", *Plant Physiology* 119, 153-164.

Lee, H.-Y., Ryu, S., Kang, H., Jun, Y.-W., and J. Cheon. 2006. "Selective catalytic activity of ball-shaped Pd@CM-48 nanocatalysts", *Chemical Communications*, 12, 1325-1327.

Li, T.S., Zhang, Z.-H., and T.-S. Jin. 1999. "Montmorillonite clays catalysis. IX. A mild and efficient method for removal of tetrahydropyranyl ethers", *Synthetic Communications*, 29(2), 181-188.

Lu, Q., Zhang, Y., Tang, Z., Li, W.-Z., Zhu, Z.-F. 2010. "Catalytic upgrading of biomass fast pyrolysis vapors with zirconia/titania based catalysts", *Fuel* 89, 2096-2103.

Mahdavi, B., LaFrance, A., Martel, A., Lessard, and H. Ménard. 1997. "Electrocatalytic hydrogenolysis of lignin model dimers at Raney nickel electrodes", *J. Appl. Electrochem.* 27, 605-611.

Meshram, H.M., Sumithra, G., Reddy, G.S., Ganesh, Y.S.S., and J.S. Yadav, J.S. 1999. "Microwave thermolysis. V. A rapid and selective method for the cleavage of THP ethers, acetals and acetonides using clay supported ammonium nitrate "Clayan" in dry media", *Synthetic Communications*, 29(16), 2807-2815.

Nikalje, M.D., Phukan, P., and A. Sudalai. 2000. "Recent advances in clay-catalyzed organic transformations", *Organic Preparations and Procedures International*, 32(1), 1-40.

Nishimura, S. 2001. "Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis", Wiley-VCH, New York.

Osada, M., Takafumi, S., Watanabe, M., Adschiri, T., and K. Aria. 2004. "Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water", *Energy and Fuels* 18, 327-333.

Perlack, R.D., Wright, L.L., Turhollow, A.F., Graham, R.L., Stokes, B.J., and D.C. Erbach. 2005. "Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply", US Department of Energy, US Department of Agriculture, DOE/GO-102005-2135, ORNL/TM-2005/66, April 2005.

Phelps, T.J., Palumbo, A.V., Bischoff, B.L., Miller, C.J., Fagan, L.A., McNeilly, M.S., and R.R. Judkins. 2008. "Micron-pore-sized metallic filter tube membranes for filtration of particulates and water purification", *J. Microbiological Methods* 74(1), 10-16.

Serio, M.A., Charpenay, S., Bassilakis, R., and P.R. Solomon. 1994. "Measurement and modeling of lignin pyrolysis", *Biomass and Bioenergy* 7, 107-124.

Shore, S.G., Ding, E., Park, C., and M.A. Keane. 2004. "The application of $\{(DMF)_{10}Yb_2[TM(CN)_4]_3\}$ (TM=Ni,Pd) supported on silica to promote gas phase phenol hydrogenation", *J. Molecul. Cat. A: Chemical* 212, 291-300.

Stamires, D., O'Connor, P., and E.J. De Graff. 2006. "Hydrocarbon Conversion Process Using Nanosized Particles, World Intellectual Property Organization", Patent WO 2006/021575 A2, 2 March.

Tang, Z., Zhang, Y., and Q. Guo. 2010. "Catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol", *Ind. Eng. Chem. Res.* 49, 2040-2046.

Thomas, J.M. 1999. "Design, synthesis, and in situ characterization of new solid catalysts", *Angew.Chem. Int. Ed.* 38, 3588-3628.

Tian, M., Wen, J.L., MacDonald, D., Asmussen, R.M., and A.C. Chen. 2010. "A novel approach for lignin modification and degradation", *Electrochemistry Communications* 12(4), 527-530.

Vermeiren, W. and J.-P. Gilson. 2009. "Impact of zeolites on the petroleum and petrochemical industry", *Top Catal.* 52, 1131-1161.

Wildschut, J., Iqbal, M., Mahfud, F.H., Cabrera, I.M., Venderbosch, R.H., and H.J. Heere. 2010. "Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst", *Energy and Environmental Science* 3, 962-970.

Wilson, K., and J.H. Clark. 2000. "Solid acids and their use as environmentally friendly catalysts in organic synthesis", *Pure Appl. Chem.* 72(7), 1313-1319.

Yakovlev, V.A., Khromova, S.A., Sherstyuk, O.V., Dundich, V.O., Ermakov, D. Yu.,

Novophasina, V.M., Lebedev, M. Yu., Bulavchenko, O., and V.N. Parmon. 2009. "Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel", *Catalysis Today* 144, 362-366.

Yan, N., Zhao, C., Dyson, P., Wang, C., Liu, L., and Y. Kou. 2009. "Selective degradation of wood lignin over noble-metal catalysts in a two step process", *ChemSusChem*. 1(7), 626-9.

Zakzeski, J., Bruijinincx, P.C.A., Jongerius, A.L., and B.M. Weckhuysen. 2010. "The catalytic valorization of lignin for the production of renewable chemicals", *Chem. Rev.* 110(6), 3552-3559.

Zhang, R., Yang, W., Xue, J. and B. Chen. 2009. "Role of Structural Deficiency of Nanoscaled Perovskites, Prepared by Reactive Grinding on the Catalytic Purification of Exhaust Pollutants," *International Journal of Chemical Reactor Engineering: Vol. 7: A49*. Available at: <http://www.bepress.com/ijcre/vol7/A49>

Zhu, J.Y., Pan, X., and R.S. Zalesny, Jr. 2010. "Pretreatment of woody biomass for biofuel production: energy efficiency, technologies, and recalcitrance", *Appl. Microbiol. Biotechnol.* 87, 847-857.

Zhu, J.Y., and X.J. Pan. 2010. "Woody biomass pretreatment for cellulosic ethanol production. Technology and energy consumption evaluation", *Bioresource Technology* 101(13), 4992-5002.

INTERNAL DISTRIBUTION

1. C. Blue
2. D. DePaoli
3. J. Gluckstein
4. M. Hu
5. M. Kidder
6. J. McFarlane
7. C. Narula
8. H. Rogers
9. M. Sturgeon
10. ORNL Office of Technical Information
and Classification

EXTERNAL DISTRIBUTION

11. Joe Renk, US Department of Energy, National Energy Technology Laboratory, Office of Project Management, 626 Cochrans Mill Road, PO Box 10940, Pittsburgh, PA 15236
12. Gideon Varga, US Department of Energy – Industrial Technologies Program, Room 5F-065, MS EE-2F, 1000 Independence Ave., SW, Washington, DC 20585