2015

Hydrogenation of Phenolic Oligomers in Bio-Oil

Zachary H. Spangler

Follow this and additional works at: http://digitalcommons.esf.edu/honors

Part of the Environmental Sciences Commons, and the Materials Chemistry Commons

Recommended Citation


This Thesis is brought to you for free and open access by Digital Commons @ ESF. It has been accepted for inclusion in Honors Theses by an authorized administrator of Digital Commons @ ESF. For more information, please contact digitalcommons@esf.edu.
Hydrogenation of phenolic oligomers in bio-oil

By

Zachary H. Spangler
Candidate for Bachelor of Science
Department of Chemistry
With Honors

May 2015

APPROVED

Thesis Project Advisor: ______________________________
Neal Abrams, Ph.D.

Second Reader: ______________________________
Jesse Bond, Ph.D.

Honors Director: ______________________________
William M. Shields, Ph.D.

Date: ______________________________
Abstract

Increasing pressure from economic, environmental, and regulatory drivers is motivating research into bio-derived liquid fuels for transportation as well as other applications. Fast pyrolysis of biomass has shown potential as a means to produce biofuels. However, pyrolytic oils are acidic and viscous, properties which our current infrastructure is not equipped to handle. Traditionally, hydrotreating of fossil oil is used to decrease viscosity and increase the energy content of the fuel. These methods are energy intensive and may not be necessary for the more oxygen rich and reactive pyrolytic oil. Previous work has demonstrated the potential of mild condition hydrogenation for improving the properties of the bio-oil but only at bench scale in a batch reactor. This work expands upon this basis by using a small scale flow through hydrogenation apparatus (H-Cube Pro, ThalesNano, Hungary). Hydrogenation conditions were varied with respect to the amount of hydrogen present, amount of catalyst, temperature, and pressure of reaction. Final products were analyzed with reference to ASTM standards. These conditions were manipulated to minimize the dynamic viscosity and modified acid number (MAN) of the product. The oil hydrogenated under optimal conditions showed improve energy content, decreased water content, decreased viscosity, and an increased MAN. Products were also analyzed by $^1$H NMR and demonstrated expected changes in functional groups.
# Contents

Acknowledgments.................................................................................................................. i  
Introduction............................................................................................................................. 1  
  Fast Pyrolysis ......................................................................................................................... 1  
  Fractionation ......................................................................................................................... 3  
  Hydrogenation ..................................................................................................................... 5  
  Study Outcomes ................................................................................................................... 8  
Methods.................................................................................................................................. 8  
  Sample Preparation .............................................................................................................. 8  
  Hydrogenation ..................................................................................................................... 9  
  Experimental Design ........................................................................................................... 10  
  Acidity .................................................................................................................................. 10  
  Viscosity .............................................................................................................................. 11  
  Elemental Analysis ................................................................................................................ 11  
  Bomb calorimetry ................................................................................................................ 12  
  Water Content – Karl Fischer ............................................................................................... 12  
  $^1$H NMR ............................................................................................................................ 12  
  Chromatography .................................................................................................................. 13  
Results and Discussion ............................................................................................................ 14  
  Condition optimization ......................................................................................................... 14  
  Functional Group Changes ................................................................................................... 15  
  Product Characterization ..................................................................................................... 17  
    Viscosity .......................................................................................................................... 18  
    Acidity ............................................................................................................................. 19  
    Elemental Analysis ........................................................................................................... 19  
    Bomb Calorimetry ........................................................................................................... 19  
    Water Content .................................................................................................................. 20  
    Chromatography ............................................................................................................. 21  
  Synthesis of Results ............................................................................................................ 22  
Conclusions.............................................................................................................................. 24  
References................................................................................................................................. 26  
Appendix................................................................................................................................. 29
Figures
Figure 1: Schematic representation of fast pyrolysis and fractionation system showing alternating condensers and ESPs. ................................. 3
Figure 2: The H-Cube by Thales Nano is a lab scale flow through hydrogenation instrument with automated controls. ............................... 7
Figure 3: Hydrogenation of SF2 - PO showed that ambient pressure minimized or had no effect on viscosity and acidity (MAN). .................................................. 15
Figure 4: Bio-oil hydrogenated under optimal conditions showed an increase in aliphatic functional groups relative to the phenolic oligomer starting material. ........................................... 16
Figure 5: Left: The viscosity of the SF2 - PO, HPO, and POC showed unexpected increases. Right: The MAN was lowest for the SF2 - PO while the SF2 - PO, HPO, and POC were indistinguishable with respect to TAN. (Error bars show 95% CI). ........................................................................................................ 18
Figure 6: The energy content (MJ/kg) was highest for the SF2 - HPO as compared to the POC and PO. (Error bars show the 95% CI). ........................................................................... 19
Figure 7: Water content analysis shows unexpected loss of water in the SF2 - HPO and POC. (Error bars show 95% CI). .................................................. 20
Figure 8: Gel permeation chromatography of SF2 - PO, HPO, and POC showed slight decrease in molecular mass. .................................................. 22

Tables
Table 1: Compositional analysis of biomass, bio-oil derived from the same biomass, and crude fossil oil from the United Arab Emirates. .................................................. 5
Table 2: Chemical shift ranges for specific functional groups in pyrolytic bio-oil. .................................................................................. 13

Appendix Figures
Appendix Figure 1: Graphs depicting the response of acidity and viscosity to the three variable conditions, solid lines represent the model result while dashed lines are the upper and lower bounds at 95% confidence. .................................................. 29
Appendix Figure 2: An example gas chromatogram (FID detector) from SF2 - HPO bio-oil showing the large number of unique peaks and difficulty in separation due to chemical similarity. .................................................. 30
Appendix Figure 3: An example 1HNMR spectrum for a hydrogenated sample of SF2 bio-oil. DMSO-d6 solvent peak is labelled and integration regions are shown. .. 30
Appendix Figure 4: A sample of structures which are representative of compounds identified as being present in bio-oil and decreasing in concentration upon hydrogenation. .................................................................................. 30
Appendix Figure 5: Proposed structure of native lignin. From Lignoworks. (2015) “What is lignin?” Retrieved 12 April 2015 from <http://www.lignoworks.ca/content/what-lignin>. .................................................. 30
Appendix Figure 6: Possible route of hydrogenation and hydrogenolysis for two model compounds, isoeugenol and vanillin. .................................................................................. 30
Acknowledgments

I would, first and foremost, like to thank the United States Department of Agriculture National Institute of Food and Agriculture (USDA NIFA) for funding this work through CenUSA BioEnergy (Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411) as well as Iowa State University (ISU) for additional funding. Any opinions, findings, results, conclusions, or recommendations presented here are solely those of the author and do not necessarily reflect the views or opinions of USDA NIFA, Iowa State University, nor the State University of New York – College of Environmental Science and Forestry (ESF).

I would also like to thank Dr. Robert Brown (ISU – Bioeconomy Institute) and his research group, especially Patrick Hall and Dr. Marge Rover for guiding and supporting this work.

Finally, I would like to thank Dr. Neal Abrams (ESF) for his advice, guidance, and support throughout my time at ESF and for reviewing this document. Last but not least Dr. Jesse Bond (Syracuse University) for inspiring my interest in thermal processing of biomass and reviewing this document.
Introduction

In the face of the numerous challenges facing the continued use of fossil derived oil (national security, availability, extraction cost, etc.) for the production of fuels and chemical commodities, natural products and biomass are being looked at as the next generation source for these materials.\(^1\) Under current paradigms, the largest use of crude oil is the production of liquid fuels (gasoline 42%, diesel 27%, jet fuel 8.9%, and other fuel oils 4.4%).\(^2\) Historically, the United States has produced a significant amount of liquid biofuels as ethanol from corn. In fact, 43% of the domestically produced corn in 2013 was used for ethanol fuel production, this is an increase from the mere 0.7% in 1980.\(^3\) Virtually all of the new corn production (marginal increase in productivity over 1980s level) has gone to fuel\(^3\). Recent regulatory measures (Renewable Fuel Standards) have mandated levels of biofuels blended with gasoline and – for the first time in 2007 – divided these mandates by the biomass used to create the fuel.\(^4\) The level of corn starch derived ethanol that could be blended with gasoline was capped at 15 billion gallons per year while requirements for the production of biomass based diesel, cellulosic biofuel, and non-cellulosic advanced biofuels grow to 21 billion gallons per year by 2022.\(^5\) This regulatory effort has sparked a great deal of new investment and research in non-traditional biofuel production pathways.

Fast Pyrolysis

Several methods exist for the conversion of biomass to useful liquid fuel products. However, the ability to process whole biomass, including the highly recalcitrant lignin complex, without costly chemical separation on the front end is a simpler, cheaper, and
less expensive approach when compared to biological processing which is selective, slow, and – for now – always run in batch reactors. Processing routes that meet these criteria are generally considered feed stock agnostic in that they treat incoming materials equivalently regardless of the source of the biomass. By definition, a feed stock agnostic process would treat whole red oak, Kraft lignin from paper birch pulping, and ground switch grass the same. Thermochemical processing strategies (gasification, fast pyrolysis, slow pyrolysis) are almost universally considered feedstock agnostic. Of the thermochemical processing methods available, fast pyrolysis yields a liquid product at high yield (~66 wt. %). Liquid products are easier to transport economically due to their typically high energy densities and the fact that liquids are easier to contain than gases and are thus desirable as a first step in the upgrading of solid biomass to biofuels. In a fast pyrolysis system, ground biomass is fed to a reactor where the biomass is heated uniformly and very quickly (up to $10^4 \, ^\circ\text{C}/\text{min}^8$, but generally significantly less) to temperatures of between 300 and 600 °C in air (~21% oxygen). This heating results in the thermal decomposition of the biomass and subsequently the volatilization of polysaccharide and lignin decomposition products (e.g. monomer and low molecular weight oligomers). These monomers and oligomers can undergo further pyrolysis to give secondary decompositions products (e.g. acetic acid from acetylated hemicelluloses, vanillin and other substituted aromatics from lignin, furfural and 5-hydroxymethylfurfural from hemicelluloses). The chemical complexity of this mixture results in several hundred unique compounds distributed over a wide molecular weight range.$^9$ Additionally the pyrolysis process itself results in very little chemical removal of oxygen (deoxygenation) and consequently highly reactive oxygenated moieties
(aldehydes, alcohols, carboxylic acids, etc.) are present in the products. In most fast pyrolysis systems, the products are condensed all together as a single product mixture. This results in a liquid product that has a high concentration of water (~20%), low energy density, low pH, and very poor stability due to the large number of reactive oxygenated functional groups (e.g. carboxylic acids, hydroxyls, and esters). While fast pyrolysis may offer the best initial treatment of raw biomass, the product is in need of improvement.

Fractionation

Most chemical upgrading strategies and therefore the total value derived from bio-oil rely on the purity/chemical similarity of intermediates and products. The traditional approach, taken from petroleum refining, of fractional distillation is not useful here due to the fact that bio-oil compounds readily decompose on heating and do not easily vaporize. To work around this issue, a novel technique for separating pyrolytic oil as it is produced has been developed. This method of fractionation groups molecules based on molecular weight and boiling point through the use of sequential

Figure 1: Schematic representation of fast pyrolysis and fractionation system showing alternating condensers and ESPs.
shell-and-tube heat exchanging condensers and electrostatic precipitators. By fractionating bio-oil in this manner, approximately five unique stage fractions (SF) are obtained (see Figure 1). The water content increased from SF1 (6.6 wt. %) to SF5 (63.3 wt. %). Sugar derived compounds (e.g. levoglucosan, furans) and larger lignin derived compounds (e.g. mono and dimethoxy phenols, phenolic oligomers) were partitioned primarily to SF1 and SF2 while lighter compounds (e.g. acetic acid, ketones) were found in SF4 and SF5. The measured viscosity of the stage fractions was far higher in SF1 and SF2 than in the other stage fractions. In fact the viscosity of these fractions was so high that pumping, use, and transportation of these oils as fuels would be made very difficult. The majority of the large molecules are in SF1 and SF2, thus they are good candidates for further upgrading.

However, as previously mentioned, upgrading strategies perform better when the incoming product is homogenous and chemically similar. To this end, the sugars in SF1 and SF2 are separated from the lignin derived compounds – phenolic oligomers (PO) or pyrolytic lignin – by washing the mixture with water and centrifuging the resulting solution to yield two easily separated layers. The aqueous layer contained almost all of the sugars while the oil layer retained the pyrolytic lignin. A variety of uses have been suggested for biomass derived sugars (i.e. the pyrolytic sugars discussed here), such as biological upgrading for lipid or ethanol production. As the oil layer contains the majority of the phenolic oligomers it is referred to as such, for example SF2-PO refers to the phenolic oligomer/oil layer from the second stage fraction. Recent studies on the fast pyrolysis of lignin show that over 569 unique phenolic oligomers are formed, many through the spontaneous recombination of phenolic monomers.
Hydrogenation

Historically, the oil industry has used catalytic hydrogenation reactions in the refining of petroleum products. Such processes include hydrogenolysis reactions in the form of hydrocracking to form lighter weight compounds, hydrodeoxygenation (HDO) to remove heteroatoms (primarily O and N) and thus decrease overall reactivity. Due to its similar appearance and physical properties, much research has attempted to apply traditional oil upgrading methods to fast pyrolysis bio-oil, these efforts have been met with mixed success. However, bio-oil is wildly dissimilar to crude fossil oil with regard to chemical composition. While crude oil has been modified and stabilized by reactions that have occurred at high pressure over several millennia, the chemical composition of bio-oil is much more similar to the native biomass.\textsuperscript{9} Table 1 shows the ultimate (elemental) analysis of a crude fossil oil sample from the United Arab Emirates, compared to a bio-oil sample and its biomass source.\textsuperscript{9,16} Most notably, the highly reactive nitrogen and oxygen species compose only 1.6% of the crude oil and 39.64% of the bio-oil. As discussed before, the elevated levels of oxygen decrease the stability of bio-oil. In addition the higher reactivity increases coke formation during industrial use.\textsuperscript{17} This indicates that applying HDO technologies to bio-oil could go a long way toward removing oxygen and thus decreasing reactivity, increasing energy density, and likely decreasing some of the acidity.

| Table 1: Compositional analysis of biomass, bio-oil derived from the same biomass, and crude fossil oil from the United Arab Emirates.\textsuperscript{9,16} |
|-----------------|----------------|----------------|
|                  | Red Oak (\textit{Quercus rubrum}) | Bio-Oil | Crude Oil (UAR) |
| %C*             | 46.4           | 53.76       | 82.8          |
| %H*             | 6.4            | 5.66        | 10.8          |
| %N*             | 0.1            | 0.07        | 0.8           |
| %S*             | -              | 0.01        | 4.8           |
| %O*             | 46.8           | 39.57       | 0.8           |
| H\textsubscript{2}O (wt%) | 4.8            | 28.3        | -             |
| Ash* (wt%)      | 0.3            | 0.93        | -             |

*Expressed on dry basis.
Initial approaches used conditions similar to those used in the treatment of crude oil; high temperature, high pressure, aggressive catalysts. Early work by Baker and Elliot hydrogenated whole bio-oil at 274 °C and 140 bar over a CoMo catalyst. These conditions, which are mild in comparison to crude oil processing, resulted in a dramatic increase in viscosity (as measured at 60 °C) from 10 cP to 14,200 cP. In light of this, it is conceivable that even gentler hydrogenation conditions could prove useful by avoiding these consistent issues of increased viscosity and catalyst deactivation by coking. Additionally, process costs increase dramatically when working at high temperature and pressure, thus a low temperature low pressure (LTLP) process could significantly reduce operating costs. In this work, LTLP hydrogenation conditions are applied to heavy ends of fractionated bio-oil (specifically SF2-PO) from red oak (*Quercus rubra*) in order to determine the effectiveness of mild conditions in the removal of oxygen, decrease in viscosity, and decrease in acidity.

Previous work using similar feed material and hydrogenation catalyst found that LTLP hydrogenation conditions were effective at reducing viscosity in a benchtop, batch-mode, hydrogenation reactor. The viscosity decreased from 4,859 to 57.7 cP. However, the reality is that batch processing is costly when expanded to industrial scale and would limit the ability for bio-oil hydrogenation to fit seamlessly into existing oil refining infrastructure. It would, therefore, be of great use to know the response of bio-oil to LTLP hydrogenation in flow through apparatus with a fixed catalyst bed that more closely resembles existing infrastructure.

To achieve this mimicry at a small lab scale, this research made use of an H-Cube Pro (Thales Nano, Budapest, Hungary). The H-Cube features a flow through
hydrogenation column that is pre-packed with catalyst and can be easily replaced to change the catalyst (see Figure 2). The temperature and pressure of the reaction are controlled between 10 and 150 °C and 0 to 100 barg respectively. Hydrogen is produced by electrolysis of ultrapure water and introduced to the system at regulated flow rates between 0 and 60 mL/min. In industrial and many lab scale reactors, ensuring uniform distribution and a high level of contact between the substrate and catalyst is a large concern\(^2\), however the design of the H-Cube’s catalyst cartridge provides very efficient interaction between the oil, catalyst, and hydrogen through the use of micro-channels. The increased interaction between the phases in the catalyst cartridge leads to a greatly increased reaction rate. Additionally, the catalyst cartridge (which can be treated exactly like a separation column from a high pressure liquid chromatography system) also guards the user against the dangers inherent in the use of pyrophoric catalysts.

Figure 2: The H-Cube by Thales Nano is a lab scale flow through hydrogenation instrument with automated controls\(^3\).
Study Outcomes

This study found optimal reaction conditions, with respect to minimizing viscosity and acidity, for the LTLP hydrogenation of SF2-PO by varying reaction temperature, catalyst, hydrogen availability, and pressure in a flow through hydrogenation process. Select physical properties of the hydrogenated bio-oil were measured to determine its eligibility as a pyrolysis liquid fuel oil per ASTM D7544. Additionally, proton NMR and gas chromatography were used to give information on chemical changes and rationalize the observed physical changes. Statistics software, JMP (SAS, North Carolina) was used to interpolate optimal reaction conditions from empirical data.

Methods

Sample Preparation

Red oak (Quercus rubra) was pyrolyzed and fractionated as described above at the BioCentury Research Farm operated by Iowa State University in Boone, IA. As received, stage fraction two (SF2) contained both sugar and lignin derived compounds. These two classes of molecules were separated by mixing the oil with an equal mass of distilled water followed by centrifugation at 3000 rpm for 30 min. Complete mixing was accomplished by a mixture of vortex mixing and hand shaking augmented by heating in a 60-70 °C oven as needed. Following centrifugation, the darker colored organic layer containing phenolic oligomers was dissolved in methanol at a concentration of 10 g phenolic oligomers per 100 mL methanol (not that the total solution volume was not 100 mL). This bio-oil/methanol solution was vacuum filtered through 0.22 μm sterile filters to
prevent instrument fouling by particulates. Based on replicate filtrations, the phenolic oligomer portion of the bio-oil was found to be approximately 3% solids by weight which is in agreement with literature. The filtered solution of SF2 – PO in methanol was subsequently hydrogenated in the H-Cube. To limit spontaneous reactions in the bio-oil or microbial growth, all samples were stored at 4 °C when not in use.

Hydrogenation

Flow through hydrogenation of SF2 – PO dissolved in methanol over a fixed bed catalyst was performed using the H-Cube described above. Palladium catalysts at three different levels were used. A 30 mm 5% Pd/C, 30 mm 10% Pd/C, and 70 mm 10% Pd/C catalyst cartridges were used and contained 7, 14, and 35 mg Pd respectively according to the manufacturer provided user manual. During initial experiments, the flow rate of the solution through the apparatus and concentration of the solution were found to exhibit no significant control over the modified acid number (see below for definition of modified acid number) and dynamic viscosity. Consequently, these were held constant at 2 mL/min and 10 g PO in 100 mL MeOH respectively. In addition to the three amounts of catalyst, temperature and hydrogen availability were also varied to three levels; 25, 45, and 60 °C and 0, 6, and 15 mL/min respectively. Following the optimization of these three methods, SF2 – PO was hydrogenated at optimal temperature, H2 flow rate, and catalyst at a variety of pressures (0, 10, 25, 50, and 75 barg). Additionally, initial hydrogenation trials resulted in rampant leaking and clogging of the preinstalled filters. Consequently, the SF2 – PO in methanol solution was filtered as described above. This eliminated any reason for or validity of solids analysis in the hydrogenated product as the solids were removed prior to hydrogenation.
Following hydrogenation the solvent was removed by rotary evaporation (rotovap) in a 20-25 °C water bath under vacuum from a MaximaDry oil free vacuum pump (Fischer Scientific) capable of pulling a 75 mmHg vacuum. Rotovap was continued until no visually perceptible change occurred in the sample and no further solvent condensed (one hour or more). Samples were then transferred to vials and stored at 4 °C for later analysis. Hydrogenation products, the starting material, and an experimental control were analyzed by a variety of standard methods summarized below. The experimental control was SF2 – PO bio-oil that was hydrogenated under the conditions identified as optimal with the exception that the Pd catalyst was replaced by inert quartz.

Experimental Design

Statistical analysis software, JMP (SAS, North Carolina), was used to determine the minimal number of trials required to model the response of the acidity and viscosity of the bio-oil to the three manipulated variables. Subsequently, experimental data was used to build non-linear response curves and identify the hydrogenation conditions which minimized both the acidity and the viscosity. In order to build the model, variables were required to be continuous not discrete. This gave rise to the use of the mass equivalents of Pd in the catalyst cartridges rather than the more descriptive identifiers (14 mg Pd rather than 30 mm 10% Pd/C). Ultimately, 21 samples were used to model the effect of the various hydrogenation conditions on viscosity and acidity.

Acidity

Acidity was measured in the hydrogenated samples by measuring the modified acidity number (MAN). Total acid number (TAN) was also measured for select samples. MAN and TAN are both titrimetric methods where by a solution of the hydrogenated bio-
oil of known mass is automatically titrated to equivalence with standardized 0.1 N KOH in isopropanol. The result is reported in mg KOH equivalents per g bio-oil. Titrations were performed by a 798 MPT Titrino autotitrator (Metrohm, Herisau, Switzerland).

MAN and TAN differed only in the solvent used; for MAN analyses the solvent used was 6.25% N,N-dimethylformamide in methanol while for TAN a solution containing 50% toluene, 49.5% isopropanol, and 0.5% water was used. The difference in solvent meant that MAN does not measure acidity contributed by phenolic protons while TAN does. Titrations were standardized against propionic acid in paraffin oil.

Viscosity

Resistance to flow, or viscosity, determines the amount of energy that is needed to transport and pump liquids and is consequently of key importance when considering whether a liquid fuel is suitable for widespread use. After solvent removal by rotovap, samples were analyzed for dynamic viscosity (hereafter just viscosity) by a Brookfield viscometer. Samples were equilibrated to 80 °C before, and maintained throughout, the experiment, this being the lowest temperature that allowed for the accurate analysis of even the most viscous samples. A manufacturer supplied 500 cP standard was routinely analyzed to ensure data quality.

Elemental Analysis

Elemental composition is a key indicator of extent of hydrogenation. The carbon, hydrogen, nitrogen, and sulfur, content of each hydrogenated bio-oil sample was measured by a Vario micro cube (Elementar Analysensysteme GmbH., Germany). Due to its similarity to bio-oil in matrix and composition rice flour was used as a standard.
Bomb calorimetry

Heat of combustion is an essential characteristic of any proposed fuel. Bomb calorimetry (6400 Automatic Isoperibol Calorimeter, Parr, Illinois) was used to determine the heat of combustion of select samples as well as the SF2 – PO starting material. Benzoic acid was used as a standard and paraffin oil of known heat of combustion was used as an accelerant to ensure that the bio-oil ignited. Any samples showing residue after analysis were discarded and repeated.

Water Content – Karl Fischer

Water content of the samples was analyzed by automated Karl Fischer titration (Karl Fischer Moisture Titrator [MKS-500], Kyoto Electronics Manufacturing Co. Ltd., Japan). The fact that samples decomposed on heating to 105 °C prohibited the use of traditional gravimetric methods for water content. A minimal amount of bio-oil of known mass was dissolved in working medium and titrated to equivalence. Both ultra-pure water and 1% water in phenol were used for calibration.

$^1$H NMR

Proton nuclear magnetic resonance spectroscopy ($^1$H NMR) is a very commonly applied technique for structural analysis of pure organic compounds, however applying $^1$H NMR to highly impure mixtures requires very high spectral resolution, complex deconvolution algorithms, and corroboration by $^{13}$C NMR experiments in order to produce any meaningful information. However, for this project, it was desirable only to analyze the changes in functional groups before and after hydrogenation not identify specific compound. This was done simply by dividing the spectrum into regions based on
knowledge of the chemical shifts of protons associated with certain functional groups. Previous work established ranges over which to integrate (see Table 2).²²

<table>
<thead>
<tr>
<th>Bio-oil samples were dissolved to a consistent concentration in hexadeuterodimethyl sulfoxide (DMSO-d₆).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 2: Chemical shift ranges for specific functional groups in pyrolytic bio-oil.</strong></td>
</tr>
<tr>
<td>Chemical Shift (ppm)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>0.0 - 1.6</td>
</tr>
<tr>
<td>1.6 - 2.2</td>
</tr>
<tr>
<td>2.2 - 3.0</td>
</tr>
<tr>
<td>3.0 - 4.2</td>
</tr>
<tr>
<td>4.2 - 6.4</td>
</tr>
<tr>
<td>6.4 - 6.8</td>
</tr>
<tr>
<td>6.8 - 8.0</td>
</tr>
<tr>
<td>8.0 - 10.0</td>
</tr>
</tbody>
</table>

MNova NMR analysis software (Mestrelab Research, Spain) was used to perform the integrations as well as automated baseline and phase correction. The sharp singlet from DMSO-d6 was used to align the spectra while the two singlet peaks attributable to methanol and water were excluded from integration.

**Chromatography**

Gel permeation chromatography (GPC) was used to compare the molecular mass distribution of select samples. Samples were dissolved in tetrahydrofuran (THF) and eluted through a GPC column with 10% isopropanol in water. An Ultimate 3000 Rapid Separation LC System (Thermo Scientific Dionex) with both refractive index (RI) and UV-vis detection was used for separations.

In an attempt to see what other changes were observable, samples were analyzed by gas chromatography with a flame ionization detector (GC-FID). Bio-oil samples were dissolved in methanol and separated on a 60 m mid-polarity column (ZB-1701, Phenomenex, California). Oven temperature was ramped from 45 °C to 235 °C over the course of the 77 min run.
Results and Discussion

Condition optimization

Data collected for MAN and viscosity were fed into JMP Statistics software along with the results that temperature, hydrogen flow rate, and catalyst loading that produced each result. JMP used these data to construct a non-linear regression which allowed for the effect of two different variables acting together (or the square of a single variable) to be included. Graphs depicting the response of acidity and viscosity to the three variable conditions are shown in Appendix Figure 1, solid lines represent the model result while dashed lines are the upper and lower bounds at 95% confidence. Based on the limited number of samples, the model predictions had very large 95% confidence intervals and therefore only one of the variables could be said to be significant at the 95% confidence level (significance being defined as p<0.05). The effect of temperature on the modified acidity number was statistically significant while the effects of hydrogen flow rate and catalyst loading were close to having a significant effect on viscosity (p=0.13 and 0.15 respectively). The effects of temperature on viscosity and hydrogen flow rate and catalyst loading on acidity were not significant. It is important to note that other variables – such as catalyst loading, hydrogen flow rate, and perhaps even unmeasured parameters such as residence time or type of catalyst – may have been found to be significant had replicate trials and/or trials at intermediate levels been added to the model, however replicate trials were not performed in this set of experiments. Based on this model the temperature, hydrogen flow rate, and catalyst loading that minimized viscosity and acidity were selected; 25 °C, 7.2 mL/min, and 7 mg Pd (30 mm 5% Pd/C) respectively. For temperature, 45 °C would have minimized viscosity, however the difference in predicted
viscosity was not very large, particularly when compared to the confidence in the prediction, thus the minimization of MAN was prioritized.

After these three conditions were optimized, additional trials were conducted at these conditions over a range of pressures from 0 to 80 bar \((8 \times 10^6 \text{ Pa})\). A simple linear regression of the MAN and viscosity of the hydrogenation products from these trials showed that reactions at ambient pressure minimized both the acidity and viscosity.

Figure 3 shows these results along with 95% CI for the MAN data. While the coefficient of determination \((R^2)\) is relatively low in both cases, the overall trend decreasing toward 0 bar was sufficient to add ambient pressure to the list of optimal conditions.

![Graph showing dynamic viscosity and modified acid number vs pressure](image)

*Figure 3: Hydrogenation of SF2 - PO showed that ambient pressure minimized or had no effect on viscosity and acidity (MAN).*

**Functional Group Changes**

Analysis of proton NMR spectra was used to compare the functional groups present in hydrogenated and non-hydrogenated SF2 – PO bio-oil. While the spectra were very “messy” (i.e. filled with overlapping signals from the over 500 unique compounds), the analysis yielded valuable results pertaining to the change in functional groups as a
result of hydrogenation. Results that are easily rationalized by examining the structure of the parent material. An example spectrum is shown in Appendix Figure 3. Figure 4 shows the percent change in area of the $^1$H NMR spectrum that is attributable to various functional groups. This figure only shows the results for the oil produced at optimal conditions, however similar results were observed for all hydrogenated samples. The most dramatic change observed by NMR was the increase in peak area attributable to protons located alpha to a carbonyl or in the benzyl position.

Previous work using GC-MS identified compounds that are a result of the pyrolytic breakdown of lignin (the majority of which are fractionated to SF2 – PO). A sample of the structures of these compounds is shown in Appendix Figure 4 along with a schematic representation of the chemical structure of lignin (Appendix Figure 5). Examination of this scheme shows how, under the extreme conditions of pyrolysis, these compounds could be produced. Many of the compounds identified in bio-oil have functional groups (e.g. double bonds, and carbonyls) which are readily hydrogenated to
add a proton in the benzyl position, this includes compounds such as isoeugenol, vanillin, 3,4-dimethyl benzoic acid, acetovanillone, propenyl phenol (and its derivatives), 4-vinyl phenol as well as phenolic dimers such as 2-phenyl benzofuran. Not surprisingly, the overall content of methyl and methylene groups increased as well. It is also worth noting that the region attributed to methoxy, ether, and aldehydes decreased. This likely due to hydrogenolysis of the frequent methoxy groups ortho to the hydroxyl on many of the phenol rings as well as cleavage of other ethers. Hydrogenation of available aldehydes would also explain the decrease in aldehyde protons and simultaneous increase in aliphatic alcohols. An example pathway for the hydrogenation of two model compounds, isoeugenol and vanillin, is available in Appendix Figure 6. The small increase in methyl and methylene protons (compared to the abundance of aromatic protons) indicates no or minimal hydrogenation of aromatic rings. This is supported by the relative stability of benzene and its aromatic derivatives to hydrogenation. While benzene can be hydrogenated by aggressive catalysts (e.g. rhodium or Raney Ni), high temperature and pressure are needed for this reaction when Pd is used as the catalyst. Consequently, aromatic rings are not likely to be hydrogenated at LTLP conditions. Overall, the observed changes in functional groups confirm the chemical addition of hydrogen and matches with expectations from limited knowledge of the variety of compounds that would be expected to be present in SF2 – PO.

Product Characterization

Because the optimization model only compared samples to each other, it was important to compare the product created under optimal conditions to the starting material. In addition to the starting material (SF2 – PO), the hydrogenated phenolic
oligomers (SF2 – HPO), were compared to an experimental control. The purpose of the control was to isolate the effect of hydrogenation from the possible effects of sample preparation and handling. To this end, an equivalent sample of SF2 – PO was dissolved in methanol, filtered, run through the H-Cube at 0 barg, 25 °C, 7.2 mL/min H2 but with an inert quartz packing material similar in physical properties to the catalytically active palladium, and evaporated under reduced pressure to remove solvent. This procedure assumes that non-catalyzed hydrogenation reactions are not occurring. The phenolic oligomer control sample (SF2 – POC) was analyzed in the same manner as the SF2 – PO and HPO.

**Viscosity**

The viscosity of each of the three samples was measured. Error! Reference source not found. Figure 5 (left) shows the side by side comparison of the results. The highest viscosity was in the control with the HPO having an intermediate viscosity. It is therefore apparent that even at mild conditions, hydrogenation is effective at reducing the viscosity of phenolic oligomers derived from pyrolytic bio-oil and that a secondary cause is at play cause an increase in viscosity. The viscosity data emphasizes the necessity of

![Figure 5: Left: The viscosity of the SF2 - PO, HPO, and POC showed unexpected increases. Right: The MAN was lowest for the SF2 - PO while the SF2 - PO, HPO, and POC were indistinguishable with respect to TAN. (Error bars show 95% CI).](image-url)
the experimental control. Without it, the data would make it seem as though hydrogenation was increasing viscosity.

**Acidity**

Both the MAN and TAN were measured for the three samples. Figure 5 (right) shows these results side by side. The MAN of the PO starting material is lower than the MAN for the other two (which is statistically indistinguishable at a 95% confidence). This implies that either no change to acidity is due to the hydrogenation or that the method was not sensitive enough to detect the change. While NMR and GC results showed that hydrogenation occurred in the bio-oil, there is no proof that any of the hydrogenation was at carboxyl groups and not at double bonds, ethers, or aldehydes. Thus, it is possible that hydrogenation under these conditions did not affect the acidity. At an 85% confidence the HPO’s MAN is lower than the MAN for the control. TAN analysis of these samples yielded results that are statistically indistinguishable. MAN values are in the range of published values for this bio-oil.⁹

**Elemental Analysis**

None of the results obtained through elemental analysis for SF2 – PO, HPO, and POC were statistically differentiable.

**Bomb Calorimetry**

Energy content for the three samples fit with predictions and the method reproducibility allowed for very high accuracy. Figure 6: The energy content (MJ/kg) was highest for the SF2 - HPO as compared to the POC and PO. (Error bars show the 95% CI).
small confidence intervals. Figure 6 shows the energy content of the three samples side by side along with their 95% CI. The starting material had the lowest energy content while the hydrogenated phenolic oligomers had the highest (higher even than the control). As expected this indicates that the addition of hydrogen also increases the energy released through combustion. This is accomplished through the conversion of double to single bonds which have inherently higher heat of combustion and the relief of ring strain through hydrogenolysis. For example the hydrogenation of benzaldehyde to benzyl alcohol, styrene to ethyl benzene, and tetrahydrofuran to butanol have corresponding increase of 200, 180, and 170 kJ/mol respectively. The energy content of the HPO (22.6 MJ/kg) is roughly half that of Fuel Oil No. 1 but is consistent with previously published data. The increase of the energy density upon hydrogenating does show that hydrogenation is a promising approach for upgrading of pyrolytic bio-oil.

**Water Content**

The crux of understanding the results rests in the water content analysis. As Figure 7 shows, the water content on a wet basis of the SF2 – PO was 17.8% while the POC and the HPO were statistically indistinguishable at 95% CI (5.9% and 5.0% respectively). There is no reason that hydrogenation would remove water, thus something about the sample treatment must be leading to the decrease in water content. This is supported by the HPO and POC data.
being indistinguishable from each other and lower than the starting material. Possible reasons for this observed change are be discussed below (see Synthesis of Results).

**Chromatography**

GC – FID analysis primarily emphasized the number of unique yet very similar compounds present in this bio-oil (for chromatogram, see Appendix Figure 2). Previous work in this lab had produced a set of calibration curves for many of the more prominent peaks. Applying this calibration to the present samples yielded peak areas for the identified compounds. While, the large number of unidentified peaks gives some doubt to the accuracy of this method, a decrease in peak area from the SF2 – PO to the HPO was observed for several compounds as expected. Notably, these include 4-vinylphenol and eugenol which were also accompanied by increases in their respective hydrogenated analogues (4-ethyl phenol and 2-methoxy-4-propyl-phenol). In addition, an observed decrease in 4-allyl-2,6-dimethoxyphenol and an increase in 2-methoxy-4-propylphenol indicates both hydrogenation of the terminal alkene and hydrogenolysis of a methoxy group.

GPC is commonly used for determining changes in molecular weight and molecular mass distribution (MMD). As hypothesized, hydrogenolysis reactions would decrease the molecular mass to a degree which may be detectable via GPC. For these experiments UV-vis detection at 254 nm absorbance was selected. The retention time was converted to molecular mass based on polystyrene standards run previously on this instrument. Due to the lack of differentiable peaks, the molecular mass distribution was broken into 25 slices for integration. Figure 8 shows the overlaid GPC results. As the results resemble a bi-modal distribution, they were divided in half at a constant molecular
mass and the area in the lower half of the MMD was compared to the area of the upper half for each sample. The hydrogenated bio-oil showed a larger percentage of area in the lower half (77%) than the control and starting material (74.6% and 74.0%). This indicates that, while not extensive, the MMD did decrease upon hydrogenation. GPC analysis also allowed for the computation of the number ($M_n$) and weight averaged ($M_w$) molecular masses and the dispersity for each of the samples. In comparing the SF2 – PO and HPO, the dispersity remained constant at 1.60 while $M_w$ decreased by 22.1 g/mol to 692.7 g/mol and $M_n$ decreased by 12.9 g/mol to 432.6 g/mol. This is additional evidence of the occurrence of hydrogenolysis reactions.

**Synthesis of Results**

The fact that the POC was distinguishable from the PO in several aspects was inconsistent with what would be expected of a control sample. Several points indicate
that some secondary factor (besides hydrogenation) was influencing the properties of the HPO (and the POC). The most obvious proximate cause was the loss of water, a factor that is not reported on in recent literature using a similar feedstock and methodology but in a batch mode bench top reaction apparatus.\(^\text{19}\) By removing the very low viscosity water from the mixture the viscosity and energy content would obviously be expected to increase. Also, because much of the acid content comes from non-volatile species it is likely that increasing concentration focused more acidity in a smaller mass, thus leading to the POC’s MAN being higher than the PO’s MAN.

If loss of water is the proximate cause of changes to the non-hydrogenated control, what is the ultimate cause? In order the conduct the hydrogenations, the bio-oil oil was dissolved in methanol and subsequently rotavapped. Solvent removal was necessary for accurate determination of viscosity, however, several other analyses could have been performed prior to solvent removal. If the rotovap heating/vacuum combination were not controlled well, water could easily have been removed from the bio-oil at this stage. While water and methanol do not form a well-defined azeotrope, co-distillation does lead to loss of the higher boiling solvent, in this case water.\(^\text{25}\) An 80 mol\% solution of methanol in water boils at 67.8 °C at atmospheric pressure and contains 8% water in the vapor phase.\(^\text{26}\) When the pressure is reduced to approximately 75 mmHg, as in the rotovap, the boiling point of this mixture is reduced to approximately 22 °C, a temperature easily reached with no or minimal heating.\(^\text{27}\) In addition other low boiling compounds in the bio-oil, or even methanol produced through hydrogenolysis of methoxy groups, which were lowering the viscosity of the bio-oil could have been removed by rotovap. Because these effects were not observed in bench top low temperature, low
pressure (LTLP) hydrogenation, it is likely that it is due to incomplete sample collection from the H-Cube or – more likely – the removal of low boiling compounds via rotary evaporation and is not inherent to LTLP hydrogenation.

Conclusions

This work showed that LTLP hydrogenation of fractionated pyrolytic bio-oil is worth pursuing and has potential to be an economical method of upgrading phenolic oligomers for fuels applications. This is based on the fact that the viscosity of the HPO was lower than the POC viscosity, the energy content of the HPO was higher than energy content of the POC, and both $^1$H NMR and GC – FID showed structural changes which confirm hydrogenation.

Many unanswered questions remain in this project. Chiefly, what is the true cause of the increase in viscosity and unexpected behavior of the control? A hypothesis is posited above but requires testing. For example, detailed analysis of the gas phase effluent from the H-Cube and analysis of the methanol/hydrogenated bio-oil solution prior to solvent evaporation should be performed. This could aid in determining what, if any, role the rotovap played in the loss of light weight compounds (e.g. water, methanol, and other light hydrogenolysis products). In addition, replication of the hydrogenation trials is needed to improve the model for optimal conditions and improve the confidence intervals. One of the side goals of hydrogenation is to increase the stability of the bio-oil. As such, accelerated aging tests should be performed on bio-oil produced by the H-Cube. Finally, alternative catalysts, such as cobalt-molybdenum mixtures or the much more aggressive Raney nickel, should be testing for usefulness at LTLP conditions with bio-
oil. Raney nickel in particular is available in a catalyst cartridge for the H-cube, is a stronger catalyst (which would result in a greater degree of hydrogenation including the removal of aromatic rings), and is significantly cheaper on a dollar per gram basis. While Pd is a common and robust hydrogenation catalyst, it is costly and rare.

Overall, pyrolysis of biomass with subsequent fractionation and hydrogenation is a promising route to novel, green liquid biofuels. Development of flow through methods should be pursued to improve the economic viability of this route.
References


Appendix Figure 1: Graphs depicting the response of acidity and viscosity to the three variable conditions, solid lines represent the model result while dashed lines are the upper and lower bounds at 95% confidence.
Appendix Figure 2: An example gas chromatogram (FID detector) from SF2 - HPO bio-oil showing the large number of unique peaks and difficulty in separation due to chemical similarity.
Appendix Figure 3: An example 1HNMR spectrum for a hydrogenated sample of SF2 bio-oil. DMSO-d6 solvent peak is labelled and integration regions are shown.
Appendix Figure 4: A sample of structures which are representative of compounds identified as being present in bio-oil and decreasing in concentration upon hydrogenation.

Appendix Figure 6: Possible route of hydrogenation and hydrogenolysis for two model compounds, isoeugenol and vanillin.