Catalytic Hydroprocessing of Bio-oils of Different Types

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INTRODUCTION AND BACKGROUND

1. INTRODUCTION AND BACKGROUND

Catalytic hydroprocessing of fast pyrolysis bio-oil has been under development for nearly 40 years. One intent of the processing is to improve the fuel quality from the highly oxygenated products to a hydrocarbon mixture, which could serve as a fuel in conventional transportation systems. This thesis includes studies to advance the state of technology of bio-oil hydrotreating.

1.1. RENEWABLE FUELS FROM BIOMASS VIA FAST PYROLYSIS AND CATALYTIC HYDROTREATING

Production of liquid fuel substitutes for petroleum has been a goal of fuels from biomass research since the days following the first Arab oil embargo of 1973. Much of the effort focused on nearer term technology such as fermentation ethanol from starches and biodiesel from vegetable oils, both known widely as first generation biofuels. Fast pyrolysis gained early recognition as a potential route from lignocellulosic biomass to liquid fuel. However, the liquid was of insufficient quality for use in internal combustion engines for transportation. Upgrading studies were undertaken to remove the residual oxygen content and generate a truly marketable hydrocarbon liquid fuel.

An important conversion pathway receiving recognition was catalytic hydrotreating as shown by the process concept diagram in Figure 1.1. As could be

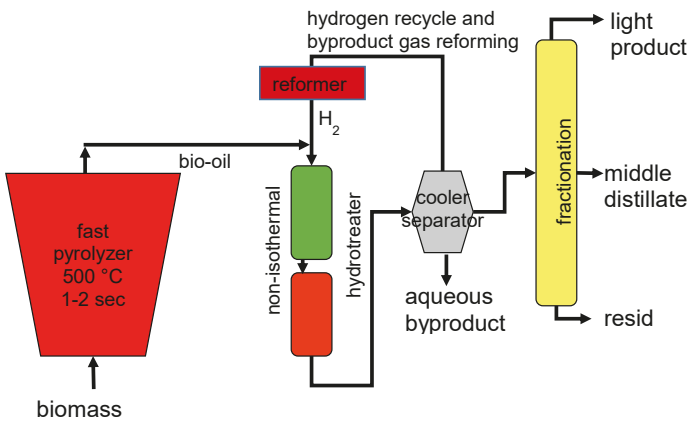


Figure 1.1. Fast pyrolysis and catalytic hydrotreating to hydrocarbon fuels

expected, the operational theory was initially developed from the commercial catalytic hydroprocessing methods for petroleum. Whereas the priority for petroleum cleanup is sulfur removal with secondary considerations of nitrogen, metals, and to some degree aromatics removal, the principle concern for bio-oil hydrotreating is the removal of oxygen, hydrodeoxygenation (HDO) with a lesser concern for sulfur and nitrogen removal along with minor trace elements carried over from the biomass source.

1.2. DEVELOPMENT OF CATALYTIC HYDROPROCESSING OF BIO-OIL AT PNNL

The early development work on fast pyrolysis bio-oil hydroprocessing at PNNL is well-described in the 2007 review by Elliott.[1] At that time, the experimentation had progressed through several continuous-flow reactor configurations involving fixed catalyst beds with either up-flow or down-flow (trickle bed) processing typically using sulfided molybdenum with either cobalt or nickel cocatalyst formulations evaluating a range of metal oxide catalyst supports with varying acidic activity. A significant development from the early work was the concept of staged temperature processing to allow for hydrogenation of less stable components in the bio-oil at lower temperature before heating the partially processed bio-oil to higher temperature to accomplish the more complete deoxygenation desired for hydrocarbon fuel production.[2]

Subsequent work at PNNL was undertaken to further develop this two-stage concept and fully overcome the catalyst bed fouling which was typical in fixed bed hydrotreating operations with bio-oil as reported by PNNL and others. A series of tests were undertaken to further validate the process and provide product and catalyst materials for analysis.[3] The low-temperature stage was studied to determine an optimum processing temperature. An alternate catalyst, Pd/C, was tested in the low temperature stage as part of this work. A range of biomass feedstocks were tested, including mixed hardwoods, corn stover, oak and poplar. The low temperature processing was evaluated over a temperature range from 310 to 360 °C and liquid hourly space velocity (LHSV)

1 D.C. Elliott, Historical Developments in Hydroprocessing Bio-oils. Energy & Fuels, 21, (2007) 1792-1815.

2 D.C. Elliott, E.G. Baker, Process for upgrading biomass pyrolyzates US Patent Number 4,795,841, issued January 3, 1989.

3 D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products, Environ Prog Sustain Energy, 28(3) (2009) 441-449.

from 0.18 to 1.14 L bio-oil/L catalyst/h. All tests were performed with a large stoichiometric excess of hydrogen in order to maintain a high partial pressure of hydrogen in the reactor operated at 13.9 MPa. The product from this initial process step was a partially deoxygenated bio-oil with O content from 12-18 wt%. This product was further processed by a second high-temperature stage using a sulfided catalyst to produce deoxygenated (<1 wt% O) products.

In addition, non-isothermal processing (combined temperature beds, Pd/C at 250 °C and sulfided catalyst at 410 °C, in one reactor) was undertaken for direct production of hydrocarbon products without intermediate recovery of partially deoxygenated products. In comparison to the independent 2-stage processing, the non-isothermal processing hydrogen consumption and hydrocarbon gas production were higher but with only minimal loss of carbon to the aqueous byproduct stream. The hydrocarbon products from the three feedstocks were similar and the source of the biomass was not readily noticeable in the product composition. An important development was the determination of reactor wall corrosion as part of the bed fouling mechanism occurring in the heat-up zone of the reactor where the acidic bio-oil components were still present.

Additional results dealing with coking mechanism, catalyst analysis, and reactor wall corrosion provided insight into coking of the catalyst in fixed-bed hydrotreating of bio-oil.[4] Coking of bio-oil was identified as a significant problem in extended operation of the hydrotreatment, often in combination with corrosion of the reactor wall. Use of the layered catalyst beds was an attempt to place a more active catalyst in the coking zone. Attempts to decouple the corrosion and coking were made by:

- use of a corrosion-resistant (coated) reactor for hydrotreating, and
- acquisition of a Hastelloy® reactor for corrosion-free hydrotreating tests.

Corrosion of the reactor wall and the thermowell had been earlier noted as a result of hydrotreating tests. The corrosion noted in those tests appeared to be associated with the zone of coke formation, i.e., toward the front end of the reactor and in the zone where the bio-oil was reaching the reaction temperature. Of course, this was the region most exposed to the bio-oil in its most acidic "primary" form before it had been reacted and been "stabilized." The composition of the coke was examined in detail in an electron microscope. Imaging of the catalyst pellets encrusted in coke provided information about

4 R. Marinangeli, E. Boldingh, S. Cabanban, Z. Fe, G. Ellis, R. Bain, D. Hsu, D. Elliott, Pyrolysis Oil to Gasoline-Final Report, PNNL-19053, Pacific Northwest National Laboratory, Richland, Washington, USA. December 31, 2014.

the elemental composition of the coke. Early on it was recognized that the metals with significant presence in the coke were nickel and iron, metals also found in the reactor wall, along with sulfur. As a result of the corrosion and the apparent link to coke formation, alternate materials were tested for the reactor wall. Type 304 stainless steel was given a corrosion resistant coating in a commercial method called Silcosteel®-CR. In another test, the reactor was fitted with a Hastelloy® liner. In this case, all fittings and tubing on the feed side were also replaced with Hastelloy units. The feed pump was not replaced as it was fabricated from nitronic 50, which is a high-nickel alloy similar to Hastelloy. Finally, a Hastelloy reactor was put into operation. However, even with corrosion resistant construction, the coke formation still occurred and was only delayed. The addition of sulfur into the reaction environment facilitated coke formation to such a degree that the advantage of a corrosion-resistant alloy construction is over-ridden.

Samples of the coke encrusted catalyst bed ("plug") were analyzed in several tests with scanning electron microscopy with electron dispersive spectroscopy. With these results the catalyst particle structures could be evaluated and elemental composition of deposits were ascertained. An analysis of the coke encrusted catalyst particle showed the Pd profile with the commercially produced edge-coating while the sulfur was distributed throughout the catalyst particle with some concentration at the edge. The reason for the visible edge-crusting was apparently a highly associated Pd and S mixture/compound. This bright edge-crust also had nickel associated with it in most cases as well as iron.

While Gagnon and Kaliaguine had reported the use of Ru as a low-temperature stabilization catalyst earlier,[5] introduction of Ru as the low-temperature stabilization catalyst in the PNNL system was initially reported in the 2004 Thermochemical Biomass Conversion Conference in Vancouver, BC, Canada presenting both model compound hydrogenation tests, as well as bio-oil hydrotreating tests.[6] Low-temperature hydrotreating at 180-240 °C was found to be effective for 30-70 % deoxygenation, but sensitivity to S poisoning at levels as low as 21 ppm in bio-oil was reported. Later collaboration with the Technical Research Centre of Finland (VTT) led to a patent application to attempt

5 J. Gagnon, S. Kaliaguine, Catalytic hydrotreatment of vacuum pyrolysis oils from wood. Ind Eng Chem Res 27 (1988) 1783-1788.

6 D.C. Elliott, G.G. Neuenschwander, T.R. Hart, J. Hu, A.E. Solana, C. Cao, Hydrogenation of Bio-Oil for Chemical and Fuel Production. In: **Science in Thermal and Chemical Biomass Conversion**, A. V. Bridgwater and D. G. B. Boocock, eds., (2006) 1536-1546, CPL Press, Newbury Berks, UK.

to capture the details of the technology for stabilizing bio-oil for long-term storage, use, and further processing of bio-oil.[7]

In addition to these works and those described in detail in this thesis, the author has also contributed three review papers to the literature summarizing the results at PNNL and elsewhere. These publications can be found as a contribution to the Wiley on-line resource for renewable energy (WIRES),[8] an opinion paper for Chemical Engineering,[9] and a book chapter.[10]

1.3. RECENT PROGRESS IN BIO-OIL HYDROTREATING IN EUROPE

The other major contributors to the literature of bio-oil hydrotreatment were members of the group functioning in Europe as the BIOCOUP project. Major participants included the University of Groningen group under Prof. Heeres and the Twente University group led by Prof. Hogendoorn.

1.3.1. BIOCOUP

The BIOCOUP was a European Integrated Project supported through the 6th Framework Programme for Research and Technological Development and was coordinated by Dr. Yrjö Solantausta at VTT. The project was aimed at developing a chain of process steps to allow a range of different biomass feedstocks to be co-fed to a conventional oil refinery to produce energy and oxygenated chemicals. Subproject #2 (SP2) dealt with deoxygenation of bio-oils and was led by the University of Twente with participation of University of Groningen, Biomass Technology Group (BTG), VTT, Aalto University, Albemarle, and the Boreskov Institute of Catalysis. The SP2 consortium aimed to develop new, integrated approaches to decrease the high oxygen content typically found in bio-oil. Pathways via thermal treatment, decarboxylation and hydrotreatment were investigated. The objectives were to develop new catalysts and produce upgraded product oils for testing in refinery processes.

7 A. Oasmaa, D.C. Elliott, Process for stabilizing fast pyrolysis oil, and stabilized fast pyrolysis oil. US Patent Appl 2012/0285079 A1, filed May 10, 2011.

8 D.C. Elliott, Transportation fuels from biomass via fast pyrolysis and hydroprocessing. **WIREs Energy Environ. 2013.** doi: 10.1002/wene.74; web published February 25, 2013.

9 D.C. Elliott, Biofuel from Fast Pyrolysis and Catalytic Hydrodeoxygenation. Current Opinion in Chemical Engineering 9, (2015) 59-65. DOI: 10.1016/j.coche.2015.08.008.

10 D.C. Elliott, Production of Biofuels via Bio-oil Upgrading & Refining. Chapter 19 in **Handbook of Biofuels' Production: Processes and Technologies** (2nd Edition), (2016) pp. 595-614. R. Luque, J. Clark, K. Wilson, C.Lin, eds., Woodhead Publishing Series in Energy, Oxford, UK.

The collaboration concluded that hydrotreatment was the only viable method of the three investigated as plain deoxygenation leads to worsening instead of improvement of the oil product properties, and the use of hydrogen thus seemed to be required, as shown through a series of studies of both high-pressure non-catalytic thermal treatment and catalytic hydroprocessing over a range of temperature.[11] The work in SP2 led to increased insights into bio-oil upgrading (as described further below) and new classes of HDO catalysts. It was concluded by the team that bio-oil stabilization by careful hydrotreatment is sufficient to produce oils suitable for co-processing, at least, in lab-scale refinery processes.[12]

1.3.2. UNIVERSITY OF GRONINGEN

Significant work on catalyst development for bio-oil hydrotreating originated at Groningen before the formation of the BIOCOUP. Heeres' group initiated their studies with model compound tests and using homogeneous Ru catalysts. Proof of principle of low temperature upgrading of bio-oil in a two-phase system was shown.[13] The group then transitioned to more conventional heterogeneous catalyst evaluation, comparing various noble metals with conventional MoS catalysts wherein they identified Ru/C and Pd/C as useful candidates[14] for low-temperature hydrotreating, at least for short-term batch reactor tests. Further work with model carbohydrate compounds led to the conclusion that Ru/C was very active even at 250 °C resulting in a large gas product, primarily methane, and that lower temperature operation, <150 °C, was suggested.[15] Batch reactions with whole bio-oil at higher temperature, 350 °C, resulted in significant gas product especially at longer residence times (>4 h) where hydrocarbon liquid product began to decrease.[16] Again, none of this work addressed the deactivation of the Ru catalyst by S and the effects

11 R.H. Venderbosch, A.R. Ardiyanti, J. Wildschut, A. Oasmaa, H.J. Heeres, Stabilization of biomass-derived pyrolysis oils, J. Chem. Technol. Biotechnol. 2010, Wiley Interscience Online, DOI 10.1002/jctb.2354.

12 Y. Solantausta, BIOCOUP Final Publishable Report, Co-processing of upgraded bio-liquids in standard refinery units, European Commission, 6th Framework Programme, contract 518312. December 7, 2011.

13 F.H. Mahfud, F. Ghijsen, H.J. Heeres, Hydrogenation of fast pyrolysis oil and model compounds in a two-phase aqueous organic system using homogeneous ruthenium catalysts. Jour Mole Catal A: Chem 264 (2007) 227-236.

14 J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind Eng Chem Res 48 (2009) 10324-10334.

15 J. Wildschut, J. Arentz, C.B. Rasrendra, R.H. Venderbosch, H.J. Heeres, Catalytic hydrotreatment of fast pyrolysis oil: Model studies on reaction pathways for the carbohydrate fraction. Environ Prog Sustain Energy, 28(3) (2009) 450-460.

16 J. Wildschut, M. Iqbal, F.H. Mahfud, I.M. Cabrera, R.H. Venderbosch, H.J. Heeres, Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst. Energy Environ Sci 3 (2010) 962-970.

on the chemical mechanisms in the reactor over time. The effects of an active Ru catalyst in its initial exposure to bio-oil do not effectively describe the mechanisms after extended use in a continuous-flow reactor. The final study before the initiation of BIOCOUP involved batch recycle tests of a range of Ru catalysts. Catalyst deactivation was reported to be a major issue. Catalyst analysis showed that clustering of metal particles and coke deposition occurred resulting in loss of active surface area.[17] However, S analysis was not undertaken and the processing results could well have occurred due to reaction of the Ru with S and resulting catalyst deactivation.

To address the perceived problem of carbon deposition on the precious metal catalyst, studies, in cooperation with Aalto University, were then undertaken with a range of metal oxide supports that were proposed to be regenerable by oxidation. The precious metals were all found to be more active than the baseline CoMo catalyst (in short 4h batch tests) and zirconia support was identified as the leading candidate as a stable precious metal catalyst support. Analysis of the spent and deactivated catalysts showed carbon deposition, which could be removed by temperature-programmed oxidation, but the catalysts were not reduced and reused to verify their activity following regeneration. The fate of the low level of S in the bio-oil was not determined but loss of S by the CoMoS catalyst was ascribed to the low (100 mg/kg) S in the bio-oil. S poisoning of the precious metal catalysts was suggested and longer term, continuous flow reactor tests were prescribed to determine catalyst activity over time.[18]

The work from the Boreskov Institue of Catalysis using supported NiCu catalysts was also brought into the BIOCOUP project and further evaluated at Groningen and BTG. The NiCu catalyst was discovered to provide an improvement over a Ni-only catalyst, allowing lower temperature (300 °C) HDO and preventing the methanation of organic oxides. Zirconia (also ceria) was identified as a useful support material, and may have provided additional activation of the catalyst. The NiCu catalyst was not used in a sulfided form and compatibility for use in low-S bio-oils was projected, but not confirmed. Comparisons of catalytic reactions with other metals and supports using model compounds are discussed by Yakovlev et al.[19] Testing at Groningen

17 J. Wildschut, I. Melián-Cabrera, H.J. Heeres, Catalyst studies on the hydrotreatment of fast pyrolysis oil. Appl Catal B: Environ 99 (2010) 298-306.

18 A.R. Ardiyanti, A. Gutierrez, M.L. Honkela, A.O.I. Krause, H.J. Heeres, Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono- and bimetallic (Pt, Pd, Rh) catalysts. Appl Catal A: General 407 (2011) 56-66.

19 V.A. Yakovlev, S.A. Khromova, O.V. Sherstyuk, V.O. Dundich, D.Yu Ermakov, V.M. Novopashina, M. Yu Lebedev, O. Bulavchenko, V.N. Parmon, Development of new catalytic systems for upgraded bio-fuels production from

suggested that titania was the preferred support for the NiCu bimetallic catalyst when used with actual bio-oil in short (3h) batch reactor tests at 350°C, following a 1h stabilization hydrotreatment at 150°C. Again, longer term continuous-flow rector tests were prescribed to better determine catalyst activity and stability.[20] Subsequent investigations of a range of Ni to Cu ratios using a δ-alumina support identified an optimum formulation, but analysis of the results showed that the activity was less than the baseline Ru/C catalyst, and leaching of the Ni, Cu and Al were significant at the reactor conditions, in contrast with the documented stability of the Ru catalyst.[21] Analysis and tracking of S was not reported.

1.3.3. UNIVERSITY OF TWENTE

Initial hydrotreating experimentation at Twente involved the use of a Ru/C catalyst (based on the Heeres group's earlier work at Groningen[12]) processing bio-oil in a 5-L batch reactor to evaluate the effects of time and temperature on product properties and to deduce an appropriate level of upgrading for coprocessing in a petroleum fluid-bed catalytic cracker (FCC).

Multiple bio-oils with different oxygen content were co-processed with petroleum streams in a lab-scale FCC unit at Shell facilities. Near-normal yields of gasoline and light cycle oil were produced without excessive coke or gas formation. Near-O-free bio-hydrocarbons were recovered.[22] Different from expected, the O content on the bio-oils was not a barrier for co-processing, while their polymerization/coking tendency was one of the critical properties.

Further study by the group attempted to define the competition between hydrotreating reactions and polymerization reactions during the hydrotreating process using small scale reactors (9-45 cm^3). Some useful results and comparisons were made, including the importance of hydrogen mass transfer rate from the bulk of the gas to the catalyst surface and hydrotreating reactions already occurring at temperatures as low as 80°C. The deactivation of the

bio-crude-oil and biodiesel. Catal Today 144, (2009) 362-366.

20 A.R. Ardiyanti, S.A. Khromakova, R.H. Venderbosch, V.A. Yakolev, I.V. Melian-Cabrera, H.J. Heeres, Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. Appl Catal A: General, 449 (2012) 121-130.

21 A.R. Ardiyanti, S.A. Khromakova, R.H. Venderbosch, V.A. Yakolev, H.J. Heeres, Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a δ-Al_2O_3 support. Appl Catal B: Environ, 117-118 (2012) 105-117.

22 F.deM. Mercader, M.J. Groeneveld, S.R.A. Kersten, N.W.J. Way, C.J. Schaverien, J.A. Hogendoorn, Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. Appl. Catal. B: Environ. 96 (2010) 57-66.

Ru/C catalyst by S in the bio-oil was not considered, but its potential effects on the relative rates of reaction were included in the discussion of results.[23]

The final contribution by the Twente group evaluated the effect of co-processing partially deoxygenated bio-oil in a hydrodesulfurization system. Both whole bio-oil and phase-separated (by water addition) bio-oil products were hydrotreated in a 0.5 L batch autoclave and the product oil subsequently co-processed with petroleum streams in a fixed bed hydrotreating system. Although the S content in the bio-oil was not measured, it was found that the O content apparently out-competed the S removal from the petroleum co-feed, such that the product resulting from co-feeding had a higher residual S level than when the petroleum stream was processed alone. The catalyst recovered full functionality when upgraded bio-oils feeding was stopped, showing that there was no permanent deactivation. The use of the Ru/C catalyst in the initial batch reactor deoxygenation step likely led to removal of most S from the bio-oil products. In the reported work, this result would not be evident as the co-fed petroleum stream had a very high level of S. But such removal would have significant effect upon further processing of whole bio-oil (undiluted) in that there would likely not be sufficient S to maintain the activity of the catalyst.[24]

1.4. THESIS OUTLINE

This thesis describes experimental work of an applied nature with a strong under-pinning of chemical mechanistic understanding, catalytic material analysis, and fuel property considerations. Based on the development of hydroprocessing technology, intermittently under development at the Pacific Northwest National Laboratory (PNNL) from 1982, the following chapters describe some of the most recent efforts in converting several types of biomass fast pyrolysis bio-oils to hydrocarbon mixtures with potential use as fuel blending components. These chapters describe bench-scale experiments in the hydroprocessing of a range bio-oil products including conventional fluid-bed pyrolysis products, hot-vapor filtered bio-oil from an entrained flow reactor,

23 F.deM. Mercader, P.J.J. Koehorst, H.J. Heeres, S.R.A. Kersten, J.A., Hogendoorn, Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. AIChE Jour 57(11) (2011) 3160-3170.

24 F.deM. Mercader, M.J. Groeneveld, S.R.A. Kersten, C. Geantet, G. Toussaint, N.W.J. Way, C.J. Schaverien, J.A. Hogendoorn, Hydrodeoxygenation of pyrolysis oil fractions: Process understanding and quality assessment through co-processing in refinery units. Energy Environ Sci 4 (2011) 985-997.

fractionated bio-oil from a conventional fluid-bed reactor as well as from an experimental system using recycled oil in the fluid-bed reactor, and finally a catalytic pyrolysis product, which is an *in situ* stabilized (deoxygenated) fast pyrolysis bio-oil product. The tests were undertaken in continuous-flow tubular fixed-bed reactors configured for trickle-bed operation with hydrogen and bio-oil both fed cold, co-currently into the top of the preheated reactor.

The preferred catalyst for HDO is a cobalt-promoted molybdenum catalyst typically formulated on a high surface area alumina (γ-Al_2O_3) support in a pelletized form.[25] The active form of the catalyst is as a sulfide. Early work with bio-oil hydrotreatment demonstrated the utility of this catalyst in continuous-flow, fixed-bed reactors. Alternatively, the nickel-promoted version was also found to be useful while favoring more hydrogenation and less deoxygenation. Process work at PNNL previous to 2009 showed a limited lifetime for the catalyst due to fouling of the catalyst bed as the temperature of the bed reached the range of 300 °C. In addition, the alumina support was known to be unstable in the high-water environment found in HDO. As a result, lower temperature operating conditions as well as alternative support materials were research targets. Chapter 2 describes research utilizing a formulation of a sulfided CoMo catalyst on carbon support as an alternative to alumina.

In Chapter 3 the hydrotreating research reverted to the use of an alumina-supported CoMo·S catalyst and involved an extended operation of the bench-scale hydrotreater to provide sufficient product material to allow the recovery by distillation of a hydrotreated (deoxygenated) bio-oil resid for use in electrode production for electrothermic metal production. In this experimental series the 2-stage hydrotreater concept was used to process the heavy (less water) phase from a phase-separated softwood pyrolysis bio-oil formed due to the feedstock being an "aged" bio-oil (over 1 year in storage) and the resulting spontaneous phase separation of the more polar and unstable components. The sulfided Co-Mo on alumina catalyst was used in both beds at both temperatures. The operating pressure of the system was 13.5 MPa. .

Chapter 4 features hydrotreating experiments involving hot-vapor filtered bio-oils produced from two different biomass feedstocks, oak and switchgrass. Hot-vapor filtering reduced bio-oil yields and increased gas yields. The yields of fuel carbon as bio-oil were reduced by ten percentage points by hot-vapor filtering for both feedstocks. The unfiltered bio-oils were evaluated alongside the filtered bio-oils using the fixed-bed catalytic hydrotreater. These tests

25 E. Furimsky, Hydroprocessing challenges in biofuels production. Catal Today 217 (2013) 13-56.

showed good processing results using a two-stage catalytic hydroprocessing strategy. Equal-sized catalyst beds, a sulfided Ru on C catalyst bed operated at 220 °C and a CoMo·S on Al_2O_3 catalyst bed operated at 400 °C were used with the entire reactor at 10 MPa operating pressure.

In Chapter 5 phenolic oils produced from fast pyrolysis of two different biomass feedstocks, red oak and corn stover were evaluated in hydrotreating tests. The phenolic oils were produced with a bio-oil fractionating process in combination with a simple water wash of the heavy ends from the fractionating process. Phenolic oils derived from the pyrolysis of red oak and corn stover were recovered with yields (wet biomass basis) of 28.7 wt% and 14.9 wt%, respectively, and 54.3 % and 60.0 % on a carbon basis. Both precious metal catalysts and sulfided base metal catalyst were evaluated for hydrotreating the phenolic oils, as an extrapolation from whole bio-oil hydrotreatment.

Continuous hydrotreating of liquid phase pyrolysis bio-oil, provided by BDI-BioEnergy International bioCRACK pilot plant at OMV refinery in Schwechat/Vienna Austria is described in Chapter 6. These tests showed promising results using catalytic hydrotreating strategies developed for unfractionated bio-oil. A sulfided base metal catalyst (CoMo on Al_2O_3) was evaluated. The bed of catalyst was operated at 400 °C in a continuous-flow reactor at a pressure of 12.1 MPa with flowing hydrogen. These tests provided the data needed to assess the quality of liquid fuel products obtained from the bioCRACK process as well as the activity of the catalyst for comparison with products obtained from hydrotreated fast pyrolysis bio-oils from fluidized-bed operation.

As described in Chapter 7, the catalytic pyrolysis oils were hydrotreated in the continuous-flow hydrotreater, operated with a single catalyst stage. Whole biomass (wood, bark and leaves from pinyon juniper) were pyrolyzed in a pilot scale bubbling, fluidized bed reactor at 450 °C and the non-condensable gases were recycled to fluidize the reactor. Red mud was used as the *in situ* catalyst for the pyrolysis. The pyrolysis products were condensed in three stages. The hydrotreater was run continuously for over 300 h with no significant catalyst deactivation or coke formation. This paper was the first time that such a long, single-stage hydrotreatment has been reported on biomass catalytic pyrolysis oils.

2

Temperature-Staged Hydrotreating of Fast Pyrolysis Bio-oil Using a C-Supported Catalyst

Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Olarte, M.V.; Zacher, A.H.; Solantausta, Y. 2012. "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust." **Energy & Fuel** *26*, 3891-3896. web published May 29, 2012.

2.1. INTRODUCTION

In terms of biomass thermochemical conversion, fast (or flash) pyrolysis is the leading method for the direct production of liquid products.[26] The liquid product of fast pyrolysis, known as bio-oil (CAS RN#1207435-39-9), has limited commercial use in production of specialty chemicals (for example, smoke flavoring), has apparent usefulness as a heavy fuel oil substitute, but its use for a transportation fuel substitute remains problematic. The bio-oil properties at issue (corrosiveness, viscosity, low energy density, thermal instability) all result from the remaining high oxygen content in the bio-oil. Removal of this oxygen content by hydroprocessing has been the subject of research over the past 25 years,[27] but it remains at a laboratory-stage of development[28] while the bio-oil production has progressed to the scale of small commercial plants.[29] Use of bio-oil as a fuel oil appears to be nearing commercial reality in the current era of higher petroleum prices. The expense of deoxygenation of the bio-oil to make it into infrastructure compatible fuels has only recently been recognized as a cost-competitive option[30] and risk reduction through scale-up of the technology remains the major hurdle.

A complicating factor in the use of fast pyrolysis bio-oil produced from softwood harvesting residues is the formation of a floating phase on top of the bulk product bio-oil.[31] The floating extractive-rich phase has been reported to account for 10 to 20 % of the bio-oil from forestry residue wherein the softwood contained significant amounts of bark and needles. It is reported to have significantly higher heating value, viscosity, and filterable solids content.

The development of technology for the application of hydroprocessing to convert bio-oil to petroleum refinery compatible feedstock remains a goal of the Department of Energy's Office of the Biomass Program. For this study the bio-oil was produced from a pine feedstock at the pilot pyrolyzer at Tampere, Finland, in collaboration of researchers from the Technical Research Center of Finland (VTT) and Metso Power. Top phase bio-oil was recovered at the VTT process development unit (PDU) at Espoo, Finland. The bio-oil products

26 S. Czernik, A.V. Bridgwater, Energy & Fuels 18 (2004) 590-598.
27 D.C. Elliott, Energy & Fuels 21 (2007) 1792-1815.
28 J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Ind Eng Chem Res 48 (2009) 10324-10334.
29 http://www.ensyn.com/products/other-product/food/
30 J. Holmgren, R. Marinangeli, P. Nair, D.C. Elliott, R. Bain, Hydrocarbon Processing 87 (9) (2008) 95-103.
31 A. Oasmaa, E. Kuoppala, S. Gust, Y. Solantausta, Energy & Fuels 17 (1) (2003) 1-12.

were shipped to PNNL and used as feedstock in continuous-flow bench-scale reactor tests in catalytic hydroprocessing. Within the project, PNNL performed hydroprocessing tests on bio-oil samples to evaluate the use of fully sulfided catalyst beds including both ruthenium and promoted molybdenum. The use of molybdenum sulfide catalysts is well known for heteroatom removal from bio-oil as well as petroleum.[32] Also considered was the report that use of ruthenium at higher temperatures would lead to excessive gas (methane) formation in the hydrogenation of bio-oil model compounds.[33] The use of sulfided ruthenium, however, has been reported for the hydrogenation of sugars and polyols without the high methane production.[34] Since the hydrogenation of the carbonyls seems to play an important role in the stabilization of bio-oil,[35] the use of RuS as a first stage catalyst was indicated.

Process conditions for catalytic hydroprocessing were derived from earlier research in bio-oil hydroprocessing.[26,36] These tests were continued over a period of time (nominally 100 hr) sufficient to achieve steady state operation and allow product samples to be recovered for analysis. The two-stage hydroprocessing strategy[37] was used to accomplish both stabilization of the bio-oil via low-temperature hydroprocessing and finished hydrocarbon product production via high-temperature hydroprocessing. Both steps were combined in a single-pass non-isothermal reactor system. Two levels of temperature were used in the catalyst bed so that both hydroprocessing steps could be accomplished without an intermediate product recovery or product separation step. The overall effect was to minimize loss and associated treatment costs of organic material in a separate aqueous phase following only partial hydrodeoxygenation. Process conditions were optimized to produce a product with low oxygen content and a low acid number.

32 E. Furimsky, Appl Catal, A: Gen 199 (2000) 147-190.

33 D.C. Elliott, T.R. Hart, Energy & Fuels 23 (2009) 631-637.

34 C. Montassier, J.C. Menezo, L.C. Hoang, C. Renaud, J. Barbier, Jour Mole Catal 70 (1991) 99-110.

35 R.H. Venderbosch, A.R. Ardiyanti, J. Wildschutt, A. Oasmaa, H.J. Heeres, Jour Chem Technol Biotechnol 85 (2010) 674-686

36 D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Environmental Progress & Sustainable Energy 28(3) (2009) 441-449.

37 D.C. Elliott, E.G. Baker, Process For Upgrading Biomass Pyrolyzates. U.S. Patent Number 4,795,841, issued January 3, 1989.

2.2. EXPERIMENTAL

The two bio-oil feedstocks for these hydroprocessing tests were shipped to PNNL by the Technical Research Center of Finland (VTT). The first (called pine, pilot in Tables 2.1-2.3) was produced in the fluid-bed fast pyrolysis pilot unit in Tampere, Finland, and the second (called pine, top phase filtered in Tables 2.1-2.3) was produced in the PDU in Espoo, Finland.

The feedstock for the pilot operation was pine sawdust, which had a moisture content of 10 wt%, volatile content of 83.4 wt%, and ash content of 0.4 wt%. The product liquid had a water content of 26 wt%. Pine was pyrolysed in the unit, which had a 2 MW pilot fluidized-bed pyrolysis reactor (7 tpd of oil) integrated to a 4 MW test fluidized-bed boiler. The product bio-oil was recovered, and stored and shipped in one cubic meter plastic containers. The feedstock for the PDU operation was harvesting residues from softwood forest. Residues had a moisture content of 9 wt%, volatile matter of 82.2 wt%, and ash content of 0.9 wt%. Harvesting residues were pyrolysed in the VTT PDU, which had a feed capacity of 20 kg/h (0.3 tpd of oil). The product oil was phase separated by standing, and an extractive-rich oil sample was recovered from the top. As recovered in Finland, the total product liquid had a moisture content of about 24 wt%, whereas the top phase moisture content was 20 wt%.

The hydroprocessing experiments were undertaken in the bench-scale hydroprocessing system in the Chemical Engineering Laboratory at PNNL in Richland, Washington, USA. That system included a fixed-bed catalytic reactor with required feeding and product recovery components. The bio-oil was mixed with a sulfiding agent, ditertiary-butyl-disulfide (DTBDS) sufficient to maintain 100 ppm sulfide in the feed and was fed to the reactor system by a high-pressure metering syringe pump. Hydrogen was introduced into the reactor via high-pressure lines and mass flow controller from a gas cylinder manifold. The fixed-bed catalytic hydrotreater (412 ml) was made from 317 stainless steel (1 inch internal diameter by 32 inches long). The bio-oil and hydrogen gas entered the top of the catalyst bed and passed downward through the bed, assumed to be in a trickle-flow. The temperature of the catalyst bed was monitored by a thermocouple, which was adjustable to various points along the center-line thermowell. After exiting the catalytic reactor, the products were cooled and collected in a dual cylinder sampling system with the uncondensed gases sampled, measured and vented. Hydrogen consumption was determined by the difference between the hydrogen gas fed (based

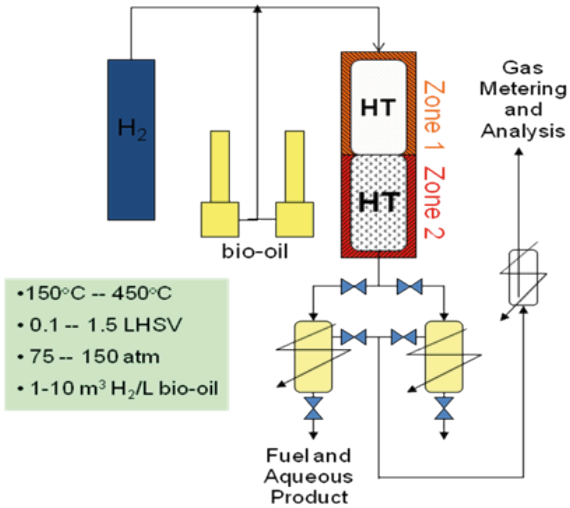


Figure 2.1. Schematic of bench-scale hydrotreater at PNNL

on the mass flow controller reading) and the hydrogen leaving the reactor as calculated by the volume measurement times the volume percent of hydrogen determined with the gas chromatograph. The recovered liquid products were phase separated, weighed and sampled for further analysis. Manually recovered gas samples were analyzed by gas chromatography. A schematic drawing of the reactor system is shown below in Figure 2.1. Mass balances varied from 95 to 105 % in various data windows during the tests with conventional bio-oil. The test with the top phase oil was relatively short and good steady-state operation was not achieved; the mass balances were less than 80 %.

A ruthenium on carbon catalyst was used in the top, low-temperature stage of the fixed-bed reactor to hydrogenate the bio-oil and produce a partially upgraded bio-oil suitable to processing at more severe hydroprocessing conditions. The Ru/C catalyst was identified in earlier experimentation for use in bio-oil upgrading.[38] It is a proprietary formulation from BASF containing well-dispersed ruthenium metal (nominally 7 wt%) on a partially graphitized carbon extrudate, 1 mm in diameter. In these experiments the temperature in the low-temperature portion of the catalyst bed was typically 170 °C and the liquid hourly space velocity (LHSV) of 0.19 L of bio-oil per L of catalyst

38 D.C. Elliott, G.G. Neuenschwander, T.R. Hart, J. Hu, A.E. Solana, C. Cao, Hydrogenation of Bio-Oil for Chemical and Fuel Production. In: *Science in Thermal and Chemical Biomass Conversion*, Bridgwater, A.V.; Boocock, D.G.B., Eds.; CPL Press, Newbury Berks, UK. (2006) 1536-1546.

Table 2.1. Elemental analysis of bio-oil feedstocks

biomass	carbon, wt%	hydrogen, wt%	oxygen, by difference	nitrogen, wt%	sulfur, wt%
pine, pilot	38.8	7.7	53.4	0.09	0.019
pine, top phase, filtered	43.9	7.6	48.2	0.26	0.036

bed per h was used. The hydrotreated bio-oil then proceeded directly into the high-temperature stage for subsequent catalytic hydroprocessing typically at 400 °C and 0.19 LHSV using a hydroprocessing catalyst. The hydroprocessing catalysts were molybdenum sulfide catalysts with cobalt promotion. For the pilot plant bio-oil tests the catalyst was one synthesized at PNNL containing 3 % cobalt and 12 % molybdenum on a carbon extrudate from Norit (ROX 0.8 mm). In the top oil test the CoMo catalyst was a fluorinated-alumina supported catalyst KF-1001 (4 wt% Co, 15 wt% Mo, 1.6 mm diameter). Both stages were operated at the same pressure of 2000 psig, nominally, with a hydrogen flow in great excess of the process requirement. Both catalyst beds were sulfided prior to the test by processing a solution of DTBDS in decane.

2.3. RESULTS

2.3.1. FEEDSTOCK DESCRIPTIONS

The bio-oil used was a pine wood derived bio-oil, which had been produced in the fluid-bed fast pyrolysis pilot plant. The bio-oil product collected actually contained a small (~1 %) top extractives rich layer, derived from the resins in the pine.**30** The first three tests described were performed with the main, bottom oil layer and a fourth test was attempted with a similar top layer recovered from pine products produced in the PDU.

In order to calculate elemental balances around the hydroprocessing experiments, the bio-oil was analyzed for carbon, hydrogen, nitrogen, and sulfur as presented in Table 2.1. The results of the analyses shown for the three samples of the pine bio-oil tested in the three experiments show the variability of the analytical result due to the inhomogeneity of the bio-oil. The nitrogen and sulfur contents of the bio-oil are highly dependent on the biomass feedstock and are relatively low in these feedstocks, as would be expected for woody biomass.

Table 2.2. Elemental Composition of Bio-oils Calculated on a Moisture-Free Basis

Biomass	H/C	Carbon, wt%	Hydrogen, wt%	Oxygen, wt%	Nitrogen, wt%	Sulfur, wt%
pine, pilot	1.43	53.0	6.4	40.5	0.1	0.03
pine, top phase, filtered	1.45	55.1	6.7	37.8	0.3	0.04

Table 2.3. Bio-oil properties

biomass	density, g/ml	TAN, mg KOH/g	viscosity, cSt @ 40°C	ash, wt %	solids, wt%
pine, pilot	1.18	72	22.6	NA	NA
pine, top phase, filtered	1.18	117	42.9	0.2	1.2

Table 2.2 shows these analyses corrected to a moisture-free basis. The moisture contents of the two bio-oils were 26.7 % for the bottom phase and 20.3 % in the top phase.

Density measurements were performed to facilitate mass balances. Total Acid Number (TAN, by ASTMD3339)) and viscosity (by ASTM D7042, includes density determination) were also analyzed. These analyses are shown in Table 2.3. The acid numbers are extremely high compared to the experience with petroleum feedstocks. The high level of oxygenates include organic acids but also phenolics, which would also be included in this analysis.[39] The ash was measured on the top phase oil and found to be not very high.

2.3.2. HYDROPROCESSING RESULTS

The hydroprocessing tests were performed in a continuous-flow reactor which was kept on stream continually until a pressure differential appeared across the fixed catalyst bed, indicating a partial plugging of the bed. Process tests with the main bio-oil used a top bed of sulfided Ru/C catalyst at ~170 °C (set point at 170 °C) and a bottom bed of sulfided promoted Mo catalyst (CoMo or NiMo) at ~400°C (set point at 390 °C), at 2000 psig with a large excess hydrogen flow at 2 standard m^3 per liter of bio-oil (10,000 SCF/bbl). The test with the top phase oil was performed with whole catalytic reactor filled with sulfided CoMo catalyst and the first portion of the bed at a set point of 250 °C. Results are given in Table 2.4 for the several tests as calculated for the indicated data windows

39 A. Oasmaa, D.C. Elliott, J. Korhone, Energy & Fuels 24 (12) (2010) 6548-6554.

Table 2.4. Time on stream effect on hydroprocessing results

test, catalyst	TOS, hr	oil yield, g/g dry feed	aqueous yield, g/g wet feed	gas yield, g/g carbon feed	hydrogen consumption, L/L feed	relative exotherm versus setpoint
HT162 NiMoS	4.5-20.6	0.35	0.51	0.21	669	7°C/22°C
HT162 NiMoS	20.6-37.1	0.38	0.54	0.27	627	3°C/22°C
HT162 NiMoS	41.5-61.6	0.39	0.53	0.24	572	3°C/23°C
HT162 NiMoS (0.08 LHSV)	81.1-89.0	0.45	0.46	0.31	545	7°C/19°C
HT163, CoMoS/C	4.1-24.8	0.35	0.52	0.25	590	5°C/15°C
HT163, CoMoS/C	24.8-57.4	0.41	0.51	0.24	545	4°C/14°C
HT163, CoMoS/C	57.4-81.0	0.39	0.52	0.26	450	4°C/14°C
HT163, CoMoS/C (0.08 LHSV)	84.9-89.1	0.37	0.53	0.30	415	2°C/14°C
HT164, CoMoS/C	7.4-23.4	0.37	0.54	0.32	503	3°C/12°C
HT164, CoMoS/C	23.4-50.4	0.40	0.54	0.31	444	3°C/13°C
HT164, CoMoS/C	66.5-82.4	0.43	0.52	0.36	342	3°C/13°C
HT166 CoMoS/Al_2O_3·F filtered top phase oil	6.3-18.3	0.42	0.39	0.14	387	12°C/20°C

represented in the Time on Stream, (TOS). The effect of time on stream can be evaluated for the pine bio-oil feedstock. The bio-oil feed rate through the two catalyst beds was 0.19 and 0.19 LHSV for a total of 0.10 LHSV through the length of the reactor. The time on stream (TOS) indicated represents time with bio-oil feed subsequent to initial catalyst sulfiding.

In these tests the yield structure was highly biased toward the aqueous layer with the combination of the water contained in the feedstock, the high water yields at low temperature and further hydrodeoxygenation and water formation at higher temperature (without intermediate water separation in these tests). The splits ranged from 1.7 to 2 times as much aqueous phase as oil phase, on a recovered mass basis. The results from Table 2.4 show a consistently higher aqueous product yield but the carbon loss was low as the carbon content in the aqueous phase was less than 0.6 wt% in all cases. Gas generation was substantial in all cases and was primarily hydrocarbons along with carbon dioxide. The very significant bed heating represented by the data in the right-most column suggested a mildly active exothermic reaction in the upper, low-temperature bed and a very more strongly effective exothermic reaction in the lower, high- temperature bed. The hydrogen consumption was very high as a combination of utilization in the saturation of double bonds,

Table 2.5. Composition of oil product from hydroprocessed bio-oils.

test, catalyst	TOS	H/C (dry)	C, wt%	H, wt%	O, wt%	N, wt%	S, wt%	TAN, mg KOH /g	moisture wt%	density g/ml
HT162 NiMoS	4.5-8.5	1.94	83.5	13.6	0.3	<0.05	0.078	<0.01	0.01	0.76
HT162 NiMoS	24.7-28.7	1.73	84.6	12.3	0.2	<0.05	<0.005	<0.01	0.01	0.80
HT162 NiMoS	45.6-57.5	1.63	86.7	11.9	0.2	<0.05	0.006	0.03	0.02	0.83
HT162 NiMoS (0.08 LHSV)	81.1-89.0	1.53	87.3	11.2	0.3	<0.05	0.014	2.7	0.03	0.87
HT163, CoMoS/C	20.8-24.8	1.77	86.2	12.8	0.3	<0.03	0.007	0.66	0.01	0.82
HT163, CoMoS/C	52.9-57.4	1.64	86.0	11.8	1.2	<0.03	0.013	<0.1	0.06	0.86
HT163, CoMoS/C (0.08 LHSV)	84.9-89.1	1.53	85.3	11.0	2.7	0.06	0.010	<0.1	0.33	0.92
HT164, CoMoS/C	7.4-19.4	1.76	84.6	12.5	0.3	<0.05	0.018	<0.1	0.01	0.82
HT164, CoMoS/C	34.7-38.4	1.59	85.0	11.4	0.7	<0.05	0.008	<0.1	0.02	0.86
HT164, CoMoS/C	70.4-82.4	1.47	84.0	10.4	2.1	0.10	0.007	<0.1	0.27	0.91
HT166 CoMoS/ Al_2O_3·F filtered top phase oil	6.3-18.3	1.56	86.5	11.4	1.5	0.17	<0.005	0.02	0.20	0.88

hydrodeoxygenation ("hydrotreating"), and hydrogenolysis of oligomeric structures ("hydrocracking"). However, there is a clear trend over time suggesting a lvoss in catalyst activity.

The chemical composition of the hydroprocessed bio-oil products are shown in Table 2.5. The composition of the bio-oils is similar for all tests. The relatively clean (low nitrogen and sulfur) pine bio-oils were converted into relatively clean hydroprocessed products.

The distillation range for some of these products was determined by simulated distillation on a gas chromatograph (ASTM D2887). Figure 2.2 shows a graphical presentation of the results for two products from the first hydroprocessing test, one from early in the test (25-29 hr TOS) and the second from later in the test (68-76 hr TOS). The shift in distillation range is obvious.

Trace element analysis of catalyst bed materials was performed by inductively-coupled plasma/optical emission spectroscopy (ICP-OES). The results are shown in Table 2.6 for catalyst samples recovered from the top catalyst bed following the test. The sulfided ruthenium is the primary component for the catalyst. The particulate mixed with the catalysts pellets, "dust," shows primarily the expected biomass mineral components—Ca, Si, Al, P, Mg, K, Cu, Na. The catalyst plug material found at the interface of the two catalyst beds,

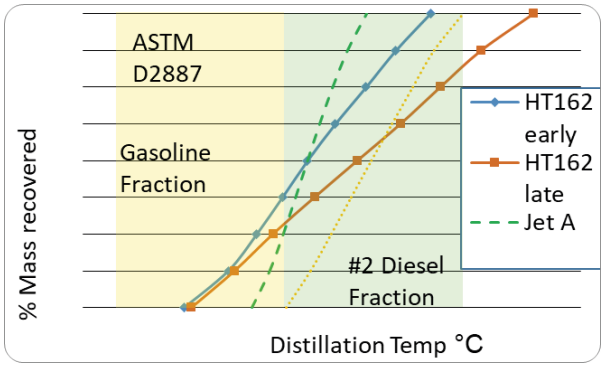


Figure 2.2. Simulated distillation of oil product from hydroprocessed pine bio-oil

Table 2.6. Trace element analysis of catalysts, mg/L

element	spent catalyst	catalyst plug	catalyst bed dust
ruthenium	36520	40850	6576
sulfur	7059	6762	2914
calcium	282	7012	52480
silicon	ND	136	44710
aluminum	396	642	5159
phosphorus	100	184	1052
magnesium	95	113	600
iron	762	916	408
potassium	578	300	1400
copper	202	176	289
sodium	ND	ND	299
titanium	20	30	29
molybdenum	287	285	300

observed to consist of catalyst pellets bound with what appeared to be a carbonaceous polymer, showed elements of both catalyst and biomass minerals.

2.4. DISCUSSION

Four hydroprocessing tests are described in this paper. In the first three, a representative bio-oil feedstock was used; in the fourth a top phase, extractive-rich

bio-oil was processed. In all four tests promoted sulfided-molybdenum catalyst was the primary hydroprocessing catalyst. In the tests with the conventional bio-oil, a preliminary hydrogenation catalyst bed composed of sulfided ruthenium on carbon was used to "stabilize" the bio-oil. This preliminary catalyst bed was not used with the extractive-rich top phase feedstock in the expectation that such bio-oil would be inherently more stable.

The intent of these tests was to surpass the 100 h barrier that has been found in earlier tests at PNNL.[40] Through those hydrotreating tests, plugging in the front end of the catalyst bed, effectively in the heat up zone, became recognized as a critical limitation to the direct hydroprocessing of bio-oil. There was little evidence of catalyst coking in the high-temperature stage. The tendency toward polymer formation (identified as thermal instability of the bio-oil) in the hydrotreating catalyst bed resulted in the buildup of pressure drop over time, ranging from 10 to 100 h depending on the operating conditions. After shutdown of the experiment a solid plug of thermosetting plastic-like material encrusted some catalyst particles in a portion of the catalyst bed, which could be recovered for analysis.

The first test reported here was stopped because of reduced activity of the catalyst bed. At 90 h on stream with bio-oil feedstock, the product quality had dropped to a level wherein the hydroprocessed oil did not readily phase separate from the water phase because the residual oxygen and increasing residual aromatic content led to emulsion formation. Upon opening the reactor it was found that there was a significant amount of dust in the upper catalyst bed and there were several pieces of catalyst fused by "coke" material at the interface of the two catalyst beds. In the second test, the catalyst activity was more stable, but the pressure-drop developed and the test was terminated at 91.5 h TOS. However, upon opening the catalytic reactor the typical hard thermoplastic-like "coked" catalyst zone was not found, but there was again a zone of packed powder with the dust in the spaces between catalyst pellets. This dust was analyzed and found to be biomass derived as opposed to catalyst disintegration product. For the 3rd test, the bio-oil feedstock was filtered prior to processing. The test was ended at 99 h TOS because of pressure drop formation. Upon opening the reactor, it was found that the dust problem persisted, but to a lesser degree. There was minimal evidence of "coke" formation in the lower (high-temperature) catalyst bed, but there was a ½ inch zone of "coke"

40 D.C. Elliott, Developments in Hydroprocessing Bio-Oil at PNNL. Presented to: *TCS 2010 Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products*, Ames, Iowa, September 22, 2010.

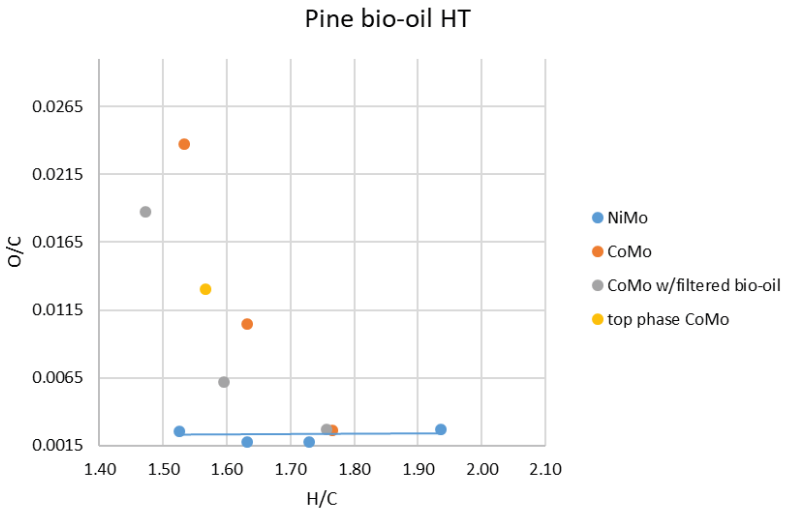


Figure 2.3. Van Krevelen plot of hydrotreated products from pine bio-oil.

at the interface of the two catalyst beds. This deposit was believed to be what produced the pressure drop that led to the test shutdown.

The chemical composition of the hydroprocessed bio-oil products was similar for all tests. The relatively clean (low nitrogen and sulfur) pine bio-oils were converted into relatively clean hydrotreated products. The use of the NiMo catalyst, compared to the CoMo catalyst, appeared to produce a more saturated product (higher H/C ratio) at the expense of higher hydrogen consumption, at least at the early time period in the run. Such a result is not unexpected in bio-oil hydroprocessing and has been reported earlier.[26]

The data demonstrate a shift in catalyst activity throughout the tests. The hydrogen consumption was very high; however, there was a clear trend over time suggesting a loss in catalyst activity. The products were essentially all hydrocarbons with a decreasing hydrogen to carbon ratio, which correlated with the lower hydrogen consumption.

For the purposes of this thesis, a van Krevelen analysis was applied to the data. As seen in Figure 2.3, the shifts in catalyst activity as a function of time on stream (almost 90 h) are evident. The curves for the CoMo data are just sight lines that suggest the trend in reduced catalyst activity for both deoxygenation and hydrogenation over the period of time on stream. The NiMo data are nearly a constant level of deoxygenation with a decreasing level of hydrogenation over time. The data point for the top phase bio-oil shows that

Table 2.7. Data from simulated distillation analysis

fraction (BP range)	HT 162 early (24.6-28.6 h TOS)	HT162 late (68.2-76.3 h TOS)
gasoline IBP-184°C	42%	33%
diesel 184-344°C	53%	43%
gas oil/resid > 344°C	5%	24%
jet A (overlap) 153-256°C	42%	40%

without the Ru catalyst, in combination with the more recalcitrant nature of the feedstock, the hydrotreating is much less effective, since the point should be near the point cluster at the end of the curves, based on TOS.

The Simulated Distillation shows that early on in the test (25-29 hr TOS) the product was essentially all gasoline and diesel range distillate (see Table 2.7). The later sample (68-76 hr TOS) showed a reduced amount of gasoline and diesel with more gasoil range and resid. The jet fuel component was only slightly less in the later sample. Quality measures of these distillate fuels were not obtained for these samples.

In all the hydroprocessing tests a 2-phase product was produced. In addition to the oil products described above, there was also a separate aqueous phase product. The aqueous phase was typically slightly contaminated with the soluble portion of the product oil. In addition to the dissolved carbon found in the water, the nitrogen and sulfur residues from the feedstock were also found. The dissolved components were likely ammonia and hydrogen sulfide byproducts of hydrotreating.

The gas products from the hydroprocessing tests were significant in amount on a carbon yield basis and typically the same composition. The main gas collected was hydrogen, as there was a great excess of hydrogen added to the reactor system to maintain a high partial pressure and facilitate its mass transfer. The main product gas components were hydrocarbons, essentially methane and ethane and on to higher carbon numbers, but at lower concentrations. There was a small amount of carbon dioxide (relative to hydrocarbons) recovered as well, typically 0.01 on a carbon basis. The excess hydrogen would be recycled and the hydrocarbon gas products would likely serve as feedstock to produce more hydrogen in the commercial application of this technology.

In order to hydroprocess the top phase, extractive-rich bio-oil, it was first filtered to remove the high level of insoluble solids. The viscosity of the bio-oil

Table 2.8. Elemental analysis of top oil phase fractions

biomass	C, wt%	H wt%	O, by difference	N wt%	ash wt%	solids wt%
centrifuged, top gel (-200 +250 mesh)	60.6	8.5	30.5	0.22	0.2	2.9
centrifuged, bottom sludge	58.7	8.4	29.7	0.22	2.9	14.1
washed solids (14.1 wt% of centrifuged bottom sludge)	59.8	4.1	17.9*	0.68	NA	100
centrifuged, filtered oil (used for hydroprocessing test feed)	43.9	7.6	48.2	0.26	0.2	1.2

* direct measurement

caused difficulties even to filter through a 100 mesh screen. Subsequent filtering through finer screens was then attempted with 200 mesh, 250 mesh, and finally 400 mesh. Centrifuging the 200 mesh filtered bio-oil facilitated the 250 mesh filtration step by removing a significant fraction of fine solids. At the 250 mesh level, the filtration recovered a gelatin-like phase. After the completed filtration/centrifugation/filtration, the final filtration at 400 mesh was relatively quick to produce the feedstock used in test HT166 (~3.6 kg out of 5.5 kg).

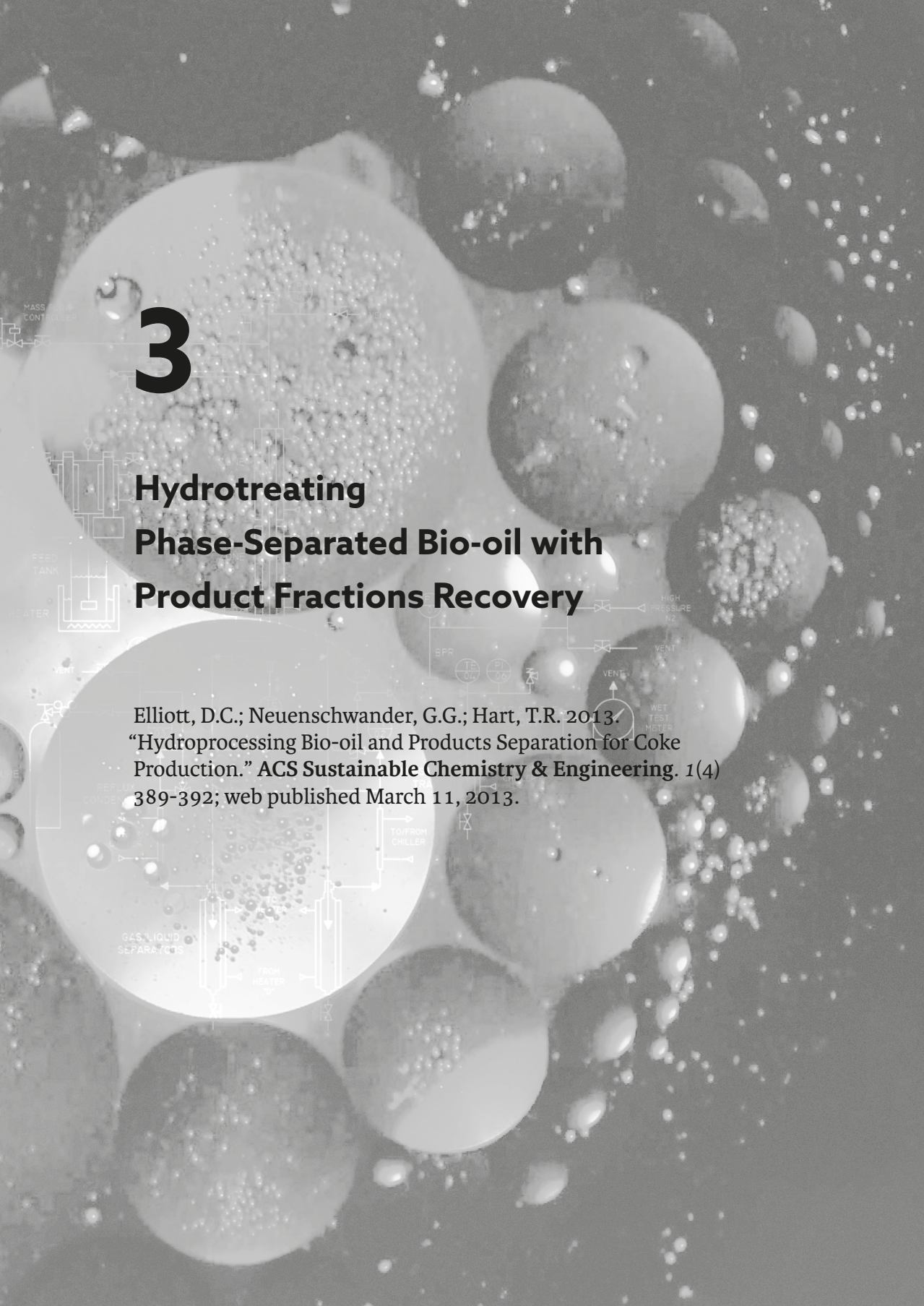
The gel recovered from the filter following the centrifugation was black and very viscous at room temperature. Upon heating to 65-70 ºC, it melted to a dark reddish-brown liquid with a viscosity more like water. Analysis of these various separated fractions from the top phase are presented in Table 2.8. The washed solids may have a large portion of ash (since the direct oxygen is much less than an oxygen by difference calculation), but there was too little sample amount recovered to do the ash measurement

After the hydroprocessing test was stopped, due to pressure drop (plugging), the reactor was opened to find that the top catalyst bed was full of brown powder even after all the preprocessing of the bio-oil feedstock. Also discovered was a ring of “coke” at the site of the highest exotherm in the lower catalyst bed. The balance of the catalyst bed was freely poured from the reactor with only a minor amount of prodding.

2.5. CONCLUSIONS

Catalytic hydroprocessing of pine fast pyrolysis bio-oils has been investigated in a bench-scale continuous-flow fixed-bed catalytic reactor system.

Incorporation of the two steps of bio-oil hydroprocessing into a non-isothermal reactor system was further explored. Effectively demonstrated was the complete processing to hydrocarbons and minimization of carbon loss in the byproduct water stream. High yields of deoxygenated hydrocarbon products were produced from the highly oxygenated bio-oil. Successful operations ranged from 90 to 99 hours on stream with conventional bio-oil. However, pressure drop increase and catalyst bed plugging resulted from hang-up in the fixed catalyst bed of char particles in the bio-oil feedstock. Pre-filtration of bio-oil products for removal of char carryover from fast pyrolysis in fluidized beds will be required for fixed-bed hydroprocessing. In the case of filtered bio-oil, catalyst bed plugging resulted from carbon fouling of the catalyst pellets at the point where the temperature was increased to the finishing hydrotreating temperature. The sulfided cobalt molybdenum on carbon catalyst appeared to have limited catalyst lifetime and exhibited deactivation over a <100 hr test. The sulfided ruthenium catalyst was used effectively here, but further optimization is required for long-term operation. The carbon supported catalysts used in these tests will not be regenerable by typical oxidative methods used with alumina supports. However, the recovery of the ruthenium metal by burning the carbon-supported catalyst is believed to be a cost effective method. The processing of the top oil, extractive-rich phase from pine bio-oil is more difficult to hydroprocess primarily because of the higher level of char solids that are difficult to remove, but also because of the mixed liquid phases.



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Hydrotreating Phase-Separated Bio-oil with Product Fractions Recovery

Elliott, D.C.; Neuenschwander, G.G.; Hart, T.R. 2013. "Hydroprocessing Bio-oil and Products Separation for Coke Production." **ACS Sustainable Chemistry & Engineering**. *1*(4) 389-392; web published March 11, 2013.

3.1. INTRODUCTION

Biomass conversion technologies provide an option for production of renewable replacements for petroleum-derived products.[41] In particular, fast pyrolysis is a useful method for high yields of liquid products from biomass.[42] Although this type of processing work was initiated in the 1980s,[43] it is only recently (past 5 years) that the effort has been restarted in earnest, since the price of petroleum has dramatically increased.[44,45] Although there have been several reviews of the field,[46,47,48,49] there remains a lack of useful data for actual processing results and in particular, processing results in continuous-flow reactors over extended periods of time.

Upgrading of bio-oil by hydroprocessing can be applied to whole bio-oil or its fractions.[50] Although bio-oil is recovered as a single phase product, it can be separated into two phases by addition of water or the separation can occur while the bio-oil is in storage wherein water might be formed by the continuing chemical reaction of the bio-oil components. It is possible to upgrade a portion of bio-oil (its heavy phase- separated portion) while using the light top phase for feedstock in hydrogen production.[51] However, the typical phase separation produces more hydrogen production feedstock than is needed to supply the hydrogen necessary for hydroprocessing of the heavy phase to liquid hydrocarbons.

41 S. Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management 45 (2004) 651-671.

42 A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 38 (2012) 68-94.

43 D.C. Elliott, Historical developments in hydroprocessing bio-oils. Energy & Fuels 21 (2007) 1792-1815.

44 D.C. Elliott, T.R. Hart, G.G. Neuenschwander, et al. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. Environ Prog & Sust Energy 28 (2009) 441-449.

45 F. deM. Mercader, M.J. Groeneveld, S.R.A. Kersten, et al. Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. Appl Catal B: Environ 96 (2010) 57-66.

46 D. Mohan, C.U. Pittman, Jr., P.H. Steele, Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels 20 (2006) 848-889.

47 G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: Chemistry, catalysis, and engineering. Chem Rev 106 (2006) 4044-4098.

48 R.H. Venderbosch, W. Prins, Fast pyrolysis technology development. Biofuels, Bioproducts & Biorefining 4 (2010) 178-208.

49 M.L. Honkela, T.-R. Viljava, A. Gutierrez, A.O. Krause, Hydrotreating for bio-oil upgrading. In *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*; Crocker, M., Ed.; RSC Publishing:Cambridge, U.K., (2010).

50 D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, M.V. Olarte, A.H. Zacher, Y. Solantausta, Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy & Fuels 26 (2012) 3891-3896.

51 T.L. Marker, J.A. Petri, Gasoline and diesel production from pyrolytic lignin produced from pyrolysis of cellulosic waste. U.S. patent 7,578,927, 25 August 2009.

Catalytic hydroprocessing of bio-oil can be used to deoxygenate the raw bio-oil and generate liquid hydrocarbon products.[42] The product quality has been studied with the intent to determine potential uses, for example as petroleum refinery feedstock.[52] In this study we consider the distillation fractions of the upgraded product with an eye on distillation resid production for generating a low-sulfur, renewable carbon electrode for metal refining.

3.2. EXPERIMENTAL SECTION

The system used in this study for hydroprocessing bio-oil was a fixed catalytic bed in a tubular reactor operated with co-current, down-flow of bio-oil and hydrogen gas (trickle-bed processing). A bench-scale unit with a 980 mL fixed catalyst bed was used for the process tests. The system is shown in Figure 3.1. The pre-heated bio-oil (at 35 to 40 °C) was fed to the reactor by a high-pressure metering syringe pump. The pump's feed cylinder and a preheater were heated by a circulating heat transfer fluid. The feed lines were all insulated to maintain temperature. The reactor was heated to operating temperature and maintained by a separate circulating, hot-oil system. The non-isothermal concept was used in these tests, which required the use of a double-jacketed reactor with one low-temperature zone and one high-temperature zone. Pressure in the reactor was maintained by a dome-loaded back-pressure regulator. Products exiting the reactor were kept warm during the collection process. The overhead product passed through a cooler which condensed out additional light components. The condensed liquids were collected in sampling cylinders, which were periodically drained. The gas product was cooled and vented through a meter, and intermittent samples were drawn for analysis. The tests were operated around the clock by trained operators using defined operating procedures specified in an approved Safe Operating Procedure. Process data was recovered manually and was also logged to the data acquisition system. A LabView control and data acquisition software was used. Samples of gas were routinely recovered and analyzed by gas chromatography.

During the tests, the heavy phase of a softwood fast pyrolysis bio-oil (containing a sulfiding agent added to maintain the sulfur level at 150 ppm or higher) was processed. A startup sulfiding operation was required with the cobalt/

52 E.D. Christensen, G.M. Chupka, J. Luecke, et al. Analysis of oxygenated compounds in hydrotreated biomass fast pyrolysis oil distillate fractions. Energy & Fuels 25 (2011) 5462-5471.

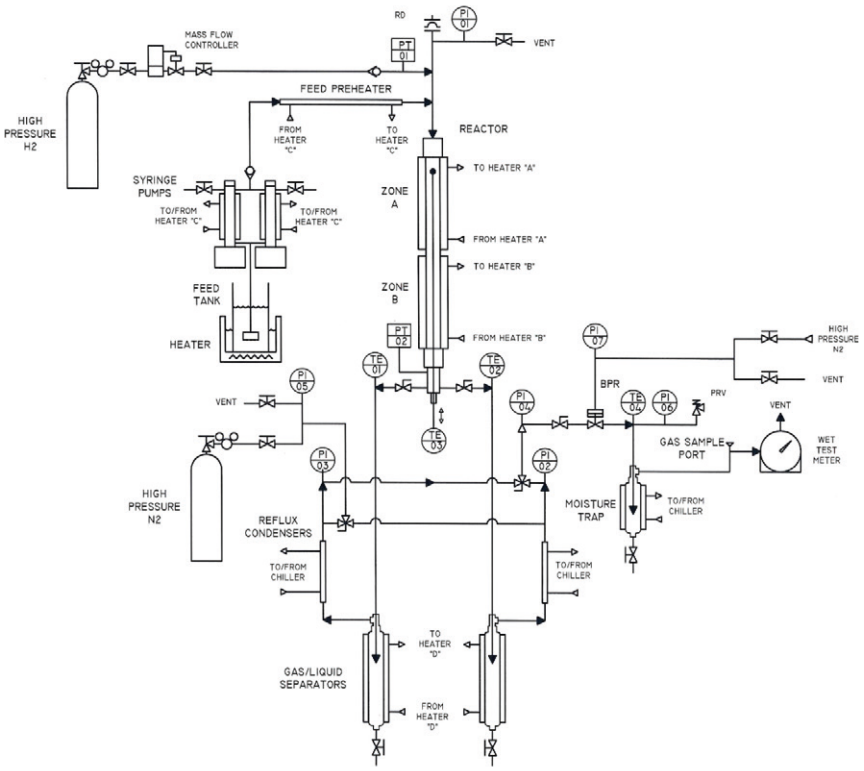


Figure 3.1. Schematic of bench-scale bio-oil hydroprocessing system

molybdenum on alumina catalyst (KAT-479 and KAT-4000) as they were received from the manufacturer (Katalco, now owned by Johnson-Matthey) in the oxide form. A solution consisting of 187.5 g di-tertiary-butyl-disulfide in 500 mL of decane was pumped through the catalyst bed at 0.1 liquid hourly space velocity (LHSV) for 1 hour at 250 °C with a subsequent period of 3 h at 380 °C. Hydroprocessing temperature set points of 250 °C in the upper (first) bed and 380 °C in the lower (second) bed were used. A significant exothermic reaction caused the catalyst beds to operate at 30 to 60 °C higher than the set points.

3.3. RESULTS AND DISCUSSION

The results of the hydroprocessing tests are presented first and discussed, followed by the results and discussion of the distillation of the upgraded bio-oil.

Table 3.1. Representative bio-oil hydroprocessing data.

	95-155 h	155-208 h	208-246 h
LHSV, liquid hourly space velocity. L bio-oil/L catalyst/h	0.15	0.14	0.14
top bed temperature, °C	244	238	232
bottom bed temperature, °C	433	448	454
operating pressure, MPa (psig)	13.3 (1918)	13.6 (1964)	13.6 (1964)
deoxygenation, %	98	99	99
mass balance, %	97	98	93
hydrogen consumption, L/L	639	502	425
product oil yield, dry wt%	55	57	58
product oil yield, vol %	68	72	71
oil yield, g C in oil/g C in bio-oil	0.81	0.80	0.80
gas yield, g C in gas/g C in bio-oil	0.17	0.17	0.16

3.3.1. HYDROPROCESSING TESTS IN THE HYDROTREATER SYSTEM

The tests were performed using the heavy phase of a softwood bio-oil. Though the product oil as produced was a single phase, the heavy phase formed from the single-phase whole bio-oil during storage and provided a convenient method to concentrate the higher-molecular weight and more aromatic components of the bio-oil. Since one goal of this study was to produce hydroprocessed bio-oil resid, the use of the heavy phase provided a more direct route to production of resid in a higher yield. The analysis of the heavy phase feedstock shows that it is significantly different from typical fast pyrolysis bio-oil, being lower in oxygen content and water, as has been reported elsewhere.[43] These tests proceeded smoothly with all reactor components functioning as designed. The process data are summarized in Table 3.1.

The tests proceeded through 4 periods lasting 95, 60, 53, and 38 h of continuous operation (246 h total). This time on stream is longer than has been reported for hydroprocessing of whole bio-oil wherein operations have been typically limited to 30 to 40 h in a similarly dimensioned vessel.[44] Those tests were limited by the increase in pressure drop across the upper portion of the catalyst bed due to fouling of the catalyst. The test periods in this work were typically stopped by pump equipment failures in the hot oil heater systems (as opposed the high-pressure bio-oil feed pump). Pressure drop buildup in the catalyst bed stopped the test at 155 h following the second session, but the deposits were attributed to an inappropriate restart procedure (resulfiding the

Table 3.2. Representative bio-oil hydroprocessing product analyses.

	feed	95-155 h	155-208 h	208-246 h
oil composition, wt%				
carbon	54.5	87.4	86.3	85.9
hydrogen	6.4	11.8	11.8	11.1
oxygen	35.5	0.6	0.6	0.6
H/C atomic ratio, dry basis	1.15	1.60	1.61	1.52
water content, wt%	10.6	0.2	0.6	0.9
density	1.25	0.87	0.89	0.90

catalyst bed without previously washing out the residual bio-oil with acetone). Fouling in the catalyst bed was found to be not a problem with this feedstock and at these operating conditions.

These processing results show the differences when using the heavy phase feedstock. Comparing to our earlier reported results,[43] the operating conditions were quite similar, considering the exothermic reaction and the hydrogen consumption. However, the product oil yield is higher and the gas yield is lower. These reflect the lower level of water in the feed and the difference in the feed composition, as it contains less of the light carbohydrate pieces (C_1 to C_4), which end up as gas upon hydrogenation, and more of the phenolic components, which can be hydroprocessed to liquid hydrocarbon products.

The product oils formed at these processing conditions were two-phased: an upper hydrocarbon phase and a lower aqueous phase with some dissolved organic components, expected to be residual unconverted phenolics. The product oil phase analyses are shown in Table 3.2. These product oils were a complex mixture much different from the feedstock bio-oil. The product properties changed slightly over the period of the run, beginning as an orange-colored oil with a density of 0.84 g/ml and ending as a dark-brown colored oil with a density of 0.90 g/ml, suggesting catalyst deactivation.

For the purposes of this thesis, a van Krevelen analysis was performed. As seen in Figure 3.2, the three data points do not suggest a relationship to time on stream, except, perhaps, to group the first two points as one then considering the shift to a lower hydrogenation toward the end of the test as an effect of time on stream. While the degree of hydrogenation varies somewhat, the deoxygenation remains stable. The extent of the test suggests a relatively stable operation using the sulfided Co-Mo catalyst when supported on alumina.

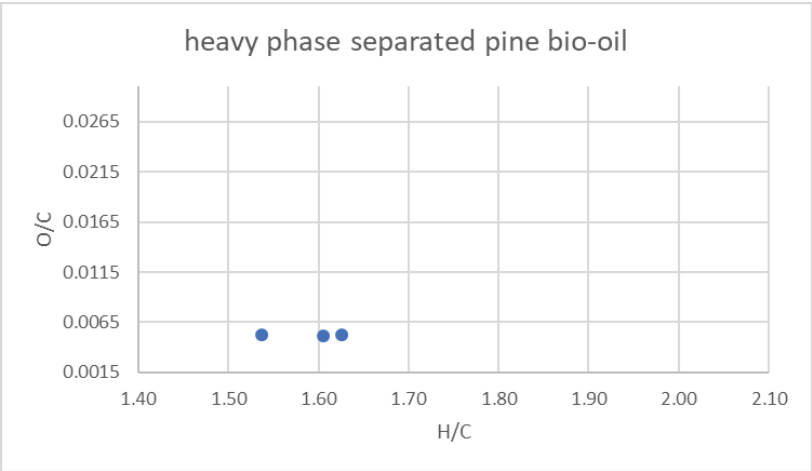


Figure 3.2. Van Krevelen plot of hydrotreated products from heavy phase-separated bio-oil

3.3.2. DISTILLATION PROCESSING OF THE HYDROPROCESSED PRODUCTS

The light hydrocarbon oil phase of the condensate product was processed through two steps of distillation to recover a residual material for coke production. First, the hydrocarbons were processed in a rotavap to strip off volatile components at a bath temperature of 100 °C at a moderate vacuum of 252 torr. The non-volatile portion was then processed through an ASTM D-1160 vacuum distillation system. Operating at 12-15 torr the still pot was run up to 410 °C.

Initial yields from the first 95 h period gave 1687 g of distillate in the rotavap with a density of 0.81 g/mL @ 22 °C. The remainder amounted to 4544 g with a density of 0.96 g/mL @ 22 °C. There was a loss of 970 g of volatiles into the vent.

After completion of all the distillations there was a total recovery of 1152 g residue (feedstock for coking and electrode production) or about 5.5 % of the product oil. Volatile products included 3.5 kg of rotovap distillate [17 %], 10.7 kg of vacuum distillate (to 380 °C pot temperature) [51 %], 586 g of vacuum distillate recovered from 380 to 410 °C (pot temperature) [3 %] and losses of volatiles (essentially all in the rotavap step) amounting to 19 %. The analyses of the recovered fractions are provided in Table 3.3.

Thermogravimetric Analysis (TGA) was applied to the resid to approximate the yield of coke that could be recovered for electrode production. The analysis of this resid shows that it is a low sulfur and low oxygen material with a high

Table 3.3. Hydroprocessed bio-oil fraction analyses.

	Rotavap	vacuum distillate	high-temp. distillate	distillation resid
oil composition, wt%				
carbon	86.0	86.5	89.7	89.6
hydrogen	13.4	12.1	11.1	10.0
oxygen	<0.3	2.3	<0.1	0.1
nitrogen	<0.06	<0.05	<0.05	0.14
sulfur	0.004	0.002	0.003	0.085
H/C atomic ratio	1.85	1.66	1.47	1.33
density, g/mL	0.81	0.94	1.02	NA

aromatic content suggested by the hydrogen to carbon atomic ratio approaching 1. Solid state ^{13}carbon nuclear magnetic resonance spectrometry of a sample of the resid provides further confirmation. Integration of that spectra showed a 71/29 split of aromatic (114 to 155 ppm chemical shift range) to aliphatic (10 to 48 ppm) for the carbons responding in the scan. TGA recovered 19 wt% of non-volatile "coke" after heating to 700 °C at 50 °C per minute. TGA of the vacuum and high-temperature distillates showed that there was little potential for coke production from the distillates. At temperatures up to 700 °C almost all the material was volatilized out of the crucible and only small amounts condensed onto the apparatus. The deposits were readily removed by dissolving in methylene chloride, suggesting little coke formation.

Gas chromatographic analysis using a mass selective detector (GC/MS) provided detailed information on the composition of the rotovap volatile components. Based on that analysis, the product oil was a mixture of aliphatic and aromatic hydrocarbons with some remaining phenolic compounds. These results are similar to those reported by other groups.[52] The aliphatics comprised 45-50 % of the product, ranging from C_4 to C_9, and included straight chain, branched, cyclic and alkyl-cyclic versions. The aromatics comprised about 40 % of the distillate and included both single and double ring (both naphthalene and indene) structures including some methyl- and ethyl-substituted versions and partially hydrogenated versions. The phenolics comprised 10 to 15 % of the distillate and included phenol and all three methyl- and ethyl-isomers, as well as C_3-phenols like methyl-ethyl compounds and propylphenol. The major components are listed in Table 3.4. The quantitation was based on the integration of the total ion chromatograph and assumes that all response factors are equal (a good assumption only for the hydrocarbons), so

Table 3.4. Major distillate products from hydroprocessed bio-oil.

compound	relative quantity	compound	relative quantity	compound	relative quantity
propylcyclohexane	5.15	toluene	3.47	phenol	2.32
ethylcyclohexane	4.60	propylbenzene	2.31	m- & p-cresol	2.26
methylcyclohexane	3.98	ethylbenzene	1.80	o-cresol	1.20
methylcyclopentane	2.03	m- & p-xylene	2.27	2,4-xylenol	0.78
cyclohexane	1.92	o-xylene	1.54	2,6-xylenol	0.72
octane	2.23	ethylmethylbenzene	1.81	2-ethyl phenol	0.70
heptane	1.33	indan	0.87	3- & 4-ethyl phenol	0.88
hexane	1.18	trimethylbenzene	0.92	propyl phenol	0.54

is only approximate.

4

Effects on Hydrotreating of Hot-Vapor Filtered Bio-oil

Elliott, D.C.; Wang, H.; French, R.; Deutch, S.; Iisa, K. 2014. "Hydrocarbon Liquid Production from Biomass via Hot-Vapor Filtered Fast Pyrolysis and Catalytic Hydroprocessing of the Bio-oil." **Energy & Fuels** *28* 5909-5917, web published: August 14, 2014, DOI: 10.1021/ef501536j.

4.1. INTRODUCTION

Fast pyrolysis of biomass is widely held to be a viable technology for the direct production of liquid fuels.[53] The bio-oil product from such processes, however, is not of sufficient quality for direct use in internal combustion engines. Catalytic hydroprocessing has been developed to convert the highly oxygenated bio-oil into hydrocarbon liquids.[54] The long-term operation of such systems has been challenging. Thermal instability of the bio-oil during the subsequent hydroprocessing, primarily in the preheating process steps has been addressed by low-temperature hydrogenations.[55] Alternatively, clean-up of the bio-oil to remove inorganic contaminants, which could act as catalysts for the thermally driven reactions, might be valuable. In addition, removal of the trace inorganics would facilitate long-term operations in the hydroprocessing reactors without catalyst fouling by inorganic deposits. Hot-vapor filtration (HVF) of biomass fast pyrolysis product has been studied at several institutions and found to effectively reduce trace element content in bio-oil by removal of char particulate.[56,57,58,59] The hot-vapor filtration has been reported to affect the bio-oil yield[58,59] and there is also reported a change in the composition of the bio-oil.[60] Such change might affect the stability of the bio-oil in subsequent heating.

The objective of this research was to evaluate physical stabilization of bio-oil, in this case by hot-vapor filtration, and its impact on catalytic upgrading to diesel, jet fuel, and gasoline. To date, the vast majority of research in hydrotreating stabilized bio-oil to produce liquid transportation fuels is centered upon stabilizing bio-oils through chemical means, including condensed phase

53 A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 38 (2012) 68–94.

54 D.C. Elliott, Historical developments in hydroprocessing bio-oils. Energy & Fuels 21 (2007) 1792-1815.

55 M.V. Olarte, D.C. Elliott, G.G. Neuenschwander, L.J. Rotness, S.D. Burton, B. Schwenzer, A. Padmaperuma, A.H. Zacher, Towards long-term fast pyrolysis oil catalytic upgrading. Prepr. Pap. Am. Chem. Soc., Div. Energy Fuels 58(2) (2013) 230-231.

56 J. Scahill, J.P. Diebold, C. Feik, Removal of residual char fines from pyrolysis vapors by hot gas filtration. in: **Developments in Thermochemical Biomass Conversion,** A.V. Bridgwater and D.G.B. Boocock, eds. Blackie Academic and Professional, London (1996) 253-66.

57 E. Hoekstra, K.J.A. Hogendoorn, X. Wang, R.J.M. Westerhof, S.R.A. Kersten, W.P.M. van Swaaij, Fast pyrolysis of biomass in a fluidized bed reactor: in situ filtering of the vapors. Ind Eng Chem Res 48(10) (2009) 4744-56.

58 A. Pattiya, S. Suttibak, Production of bio-oil via fast pyrolysis of agricultural residues from cassava plantations in a fluidized-bed reactor with a hot vapour filtration unit. Jour Anal Appl Pyrol 95 (2012) 227-235.

59 R.M. Baldwin, C.J. Feik, Energy & Fuels 27 (2013) 3224-38.

60 P.A. Case, M.C. Wheeler, W.J. DeSisto, Effect of residence time and hot gas filtration on the physical and chemical properties of pyrolysis oil, Energy & Fuels 28 (2014) 3964-3969.

(low-temperature hydroprocessing[61,62] or thermal treatment[63]) or vapor phase treatment (catalytic pyrolysis[64] or copyrolysis with chemical stabilizers[65]). Of less emphasis in the current research is physically stabilization of bio-oil, such as by filtration. This study was formulated to assess the impact on the fuel conversion process and to determine if existing barriers, particularly hydrotreating catalyst lifetime, can be mitigated through the use of physical stabilization, in this case hot-vapor filtration.

A woody and herbaceous biomass were selected as the feedstocks for this study. Hot-filtered bio-oils were produced in a fluidized-bed reactor at the National Renewable Energy Laboratory (NREL) and the impact of filtration on oil properties assessed. Pacific Northwest National Laboratory (PNNL) hydrotreated the hot-vapor filtered pyrolysis oils in a bench-scale, continuous-flow, packed-bed catalytic reactor to validate the utility for the hot-vapor filtration for fast pyrolysis bio-oil and its impact on subsequent hydroprocessing to hydrocarbon fuels. This collaboration between NREL and PNNL leverages existing expertise to assess the impact of hot-vapor filtration at NREL[56,59] on the hydrotreating process to produce liquid transportation fuels at PNNL.[61,62]

4.2. EXPERIMENTAL

4.2.1. FEEDSTOCKS

Commercial pelletized oak and switchgrass pellets from Idaho National Laboratory were knife milled through a 0.5 mm screen and used without further sizing.

4.2.2. FAST PYROLYSIS AND HOT-VAPOR FILTRATION

The feedstocks were pyrolyzed in the laboratory-built 5.0 cm (2") i.d. fluidized-bed reactor (2FBR) equipped with a glass condensation system (see

61 J. Wildschutt, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind Eng Chem Res 48 (2009) 10324-34.

62 A. Oasmaa, D.C. Elliott, Process for stabilizing fast pyrolysis oil and stabilized fast pyrolysis oil. patent application US **2012**/0285079 A1 2012.

63 M. Rep, R.H. Venderbosch, D. Assink, W. Tromp, S.R.A. Kersten, W. Prins, W.P.M. van Swaaij, De-oxygenation of bio-oils. in: **Science in Thermal and Chemical Biomass Conversion,** A.V. Bridgwater and D.G.B. Boocock, eds. CPL Press, Newbury Berks, UK (2006) 1526-35.

64 D.J. Mihalcik, C.A. Mullen, A.A. Boateng, Screening acidic zeolites for catalytic fast pyroloysis of biomass and its components. Jour Anal Appl Pyrol 92 (2011) 224-32.

65 L. Moens, R.J. French, K. Iisa, Co-hydrotreating of pyrolysis oil with hydrogen donor solvents. to be presented at TCS2014, Denver, Colorado, September 2-5, 2014.

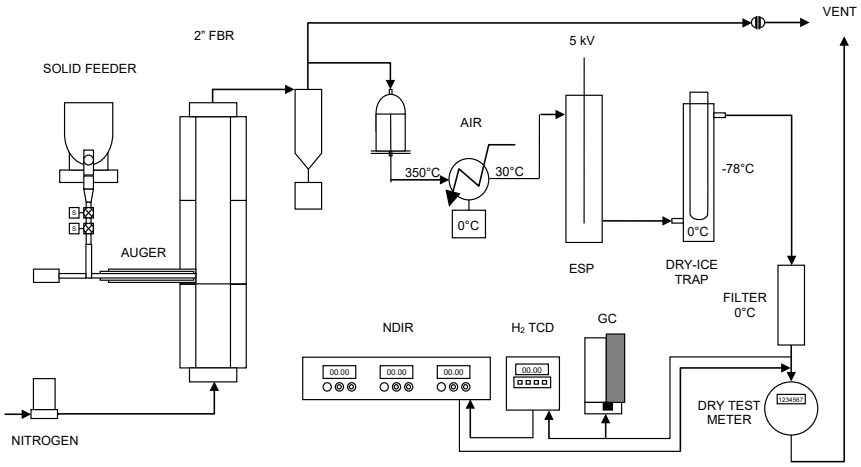


Figure 4.1. Process flow diagram for 5 cm fluidized-bed reactor with condensation system and gas measurement system.

Figure 4.1) to produce and collect the product bio-oils. The 2FBR was filled with ~300 g of 300-500 μm silica sand and fluidized with 14 L min^{-1} (standard) of nitrogen. The bed was indirectly heated by an electric furnace; the temperature was measured at three points vertically, and typically there was <10 °C variation along the bed from the nominal desired temperature. Biomass was fed at a rate of 400-500 g h^{-1} with an auger into the bed, 2 cm above the gas distributor plate. A total of 2.1 to 2.4 kg was fed for each condition.

Char was removed in the solids cyclone and for hot-vapor filtered oils fine particles were removed in the hot filter (2 μm 316 SS pleated stainless steel screen). For unfiltered oils, the filter element was removed but the empty housing remained in place, so the residence time at temperature remained constant. The pyrolysis temperature and the hot-vapor filter temperature were both 500 °C. All lines and the cyclone were heat traced and kept at 400-500 °C before the gases and vapors entered the air-cooled condenser. The calculated vapor residence time in the reactor was 0.9 s along with 1.0 s in the filter.

The condensation train consisted of two condensers and an electrostatic precipitator (ESP). The first air-cooled condenser was cooled by convection. All condensed liquids were allowed to flow into an ice-cooled, two-neck flask and the gas phase passed out of the flask to a 5 cm (2") diameter electrostatic precipitator (ESP) where aerosols were collected. The ESP was operated with a nominal +5 kV potential on the central conductor and was maintained at

ambient temperature by air cooling. Liquids that collected were drained into a 1-L collection bottle and the gas phase passed out of the ESP to a cold-finger dry-ice trap with a chilled receiver. After leaving the dry-ice trap, the gas passed through a dry-ice chilled coalescing filter into a dry test meter to measure total gas volume before venting.

A slipstream of the vent gas was fed to a bank of analytical instruments. A California Analytical Instruments Model300® NDIR system with methane, carbon monoxide, and carbon dioxide modules was used to monitor the effluent gas in real time, as was the Thermal Conductivity Monitor TCM hydrogen monitor (Gerhard Wagner). A three-channel (MS 5A x 10 m, PBQ x 10 m and CP Sil 5 x 8 m) Varian CP 4900 MicroGC was used to measure permanent gases and C_2 and C_3 hydrocarbons. The experiment was controlled by an OPTO22 system.

Oil yield was determined by weighing each piece of the condensation train before and after the experiment. Char was determined by adding the mass gained by the fluidized bed to the masses of the solids collected in the cyclone and filter. Gas yield was determined by the gas composition from the gas chromatograph and the flow as determined from the dry test meter.

The three liquids collected differed in appearance. The air condenser contained two phases—one dark and thick, and the other clear and water-like. The ESP contained a brown liquid of syrupy consistency. The dry-ice trap, after melting, contained a faintly yellow thin liquid. These three liquids were combined into one composite sample by vigorous shaking on a commercial paint shaker and then were stored at 4 °C when not in use. Prior to removing aliquots for analysis the material was allowed to warm to room temperature for 30-60 minutes and shaken by hand for one minute prior to sampling.

4.2.3. HYDROPROCESSING

The bio-oil samples produced at NREL were shipped to PNNL. The four samples included two from each feedstock (an oak wood and a switchgrass) with a sample of hot-vapor filtered and unfiltered for each feedstock. Mini-reactor hydroprocessing tests were completed on all four bio-oil samples provided by NREL.

The bio-oils were hydroprocessed in the mini-hydrotreater (see Figure 4.2). The hydrotreater was configured as a single pass, co-current, continuous, down-flow reactor. The system can operate at up to 12.4 MPa (1800 psig) with a maximum catalyst temperature 400 °C. The system consists of a gas and liquid feed system, heated reactor system, and a gas-liquid separation system.

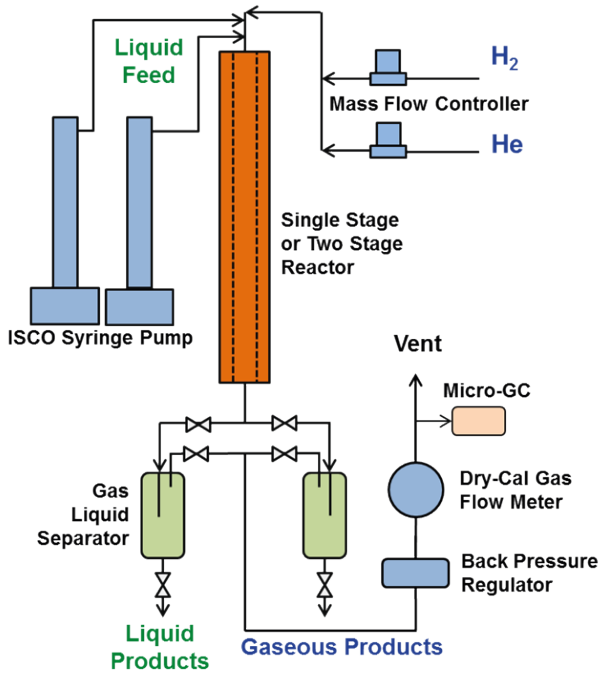


Figure 4.2. Schematic of the mini-reactor hydrotreater system

The gas feed system consists of a manifold for feeding hydrogen through one mass flow controller and helium through a second mass flow controller. The liquid bio-oil feedstocks are delivered to the pressurized reactor system by two high pressure ISCO syringe pumps. The tubular fixed-bed catalytic hydrotreater was made of 316 stainless steel (13 mm (1/2”). internal diameter by 64 cm. long with 40 ml capacity for single stage heater or 24-24 ml capacity for two–stage heater). The reactor was heated by either a single heating zone heater for single stage hydrotreating or a two heating zone heater for two stage hydrotreating. The liquid feedstock and hydrogen gas entered the top of the catalyst bed and passed downward through the bed, assumed to be in a trickle flow. The temperature of the catalyst beds was monitored by thermocouples in a thermocouple well (5 mm (3/16”) tubing). After exiting the catalytic reactor, the liquid products were separated from the gaseous products in one of two pressurized and cooled traps placed in parallel flow downstream of the reactor system. Periodic liquid samples were collected when switching collection vessels and venting/draining the trap. The recovered liquid products were phase-separated, weighed, and sampled for further analysis. The off-gas

passed through the back-pressure regulator and was then directed through a DryCal gas meter to measure gas flowrate. Periodic gas samples were analyzed by an online Inficon Micro-GC 3000 4-Channels micro gas chromatograph with molecular sieve, Plot U, Alumina, and Stabilwax columns. Prior to each hydrotreating test, the micro GC was calibrated by using a calibration gas.

Sulfided catalysts were used in the tests at two temperature levels. The tests were operated for 60 hours and were terminated as planned without plugging or equipment failure. Over the period of the tests slight, but steady, catalyst deactivation was evident based on increasing density of product and decreasing amount of hydrogen consumption with increasing yield of carbon oxides.

Each test was performed under similar conditions using the dual bed hydrotreating/ hydrocracking procedure that is the current state of the technology. Campaigns were performed for each feed over the course of a five-day test, and the products and feed were collected to assess performance for each stabilized feed type to compare to the results with the unfiltered bio-oil.

4.2.4. ANALYTICAL METHODS

The feedstocks and bio-oils as produced were analyzed at NREL. C, H, N and S contents of the bio-oils and feedstocks were measured with a LECO® TruSpec CHN+S module, and O was calculated by difference. Each sample was run in triplicate with approximately 150 mg of sample taken per determination. Proximate analysis for the feedstocks and bio-oils was conducted with a LECO TGA701 Thermogravimetric Analyzer. Each sample was run in triplicate with approximately 250 mg of sample used per determination. Water analysis was done on a Metrome® 701 Karl Fisher Titrator using methanol as the solvent and commercial Hydranal®-Composite 5 reagent as the titrant. The samples were run in triplicate with approximately 110 mg of oil used per determination

The bio-oils were analyzed for Ca, K, and Na by Huffman Laboratories, Inc. The samples were analyzed in duplicate in Teflon digestion tubes at approximately 0.1 and 0.2 g sample weights. They were then digested with nitric and perchloric acid. The completed digestion was analyzed by ICP-AES on a Perkin Elmer 5300DV instrument with excellent agreement between duplicates.

Acids and phenolics determination for the pyrolysis oils was done in a single potentiometric titration on a ~1000 mg sample dissolved in 10 mL 80 vol% ethanol. End points were determined by calculation of inflection points in the titration curve. Titrant was standardized 0.01 M NaOH in water.

Total carbonyl content was done on duplicate titrations of the hydrogen chloride released by the reaction of $MeONH_2 \cdot HCl$ with any reactive carbonyl groups. A sample of ~250 mg dissolved in 10 mL 95 vol% ethanol. A 0.5 to 2x excess of methoxy-amine is used to reach a consistent reaction endpoint. Back titration was done with 0.01 M NaOH in water.

The bio-oils and hydrotreated products were characterized at PNNL for elemental analysis including C, H, N, O, S, Total Acid Number (TAN), water content, metals content, and solids. In addition, the products were analyzed by simulated distillation (ASTM D2887) in order to assess the relative amounts of fuel products in the gasoline, diesel, jet fuel, and residual ranges.

4.3. RESULTS

4.3.1. FEEDSTOCKS

Results from the feedstock analyses are shown in Table 4.1. The main difference between the feedstocks is the ash, which was twenty times higher in switchgrass than in oak.

Table 4.1. Composition of feedstocks as fed

	proximate analysis (wt %)				ultimate analysis (wt %)				
	moisture	volatiles	fixed carbon	ash	C	H	N	S	O
oak	6.1	79.7	13.8	0.39	49.6	6.03	0.08	0.01	43.9
switchgrass	6.0	81.5	10.4	8.06	43.2	6.33	0.90	0.15	41.4

4.3.2. FAST PYROLYSIS AND HOT-VAPOR FILTRATION RESULTS

The yields of the major components (oil, char, and gas) in the fast pyrolysis experiments are shown in Table 4.2. The amounts of biomass fed, oil, and char were measured gravimetrically as weight changes in the appropriate parts of the system. For the biomass this was mass loss in the Ktron feeder; for the oil the sum of the weight changes in the liquid receivers, condensers, ESP, and the hoses in the condensation train; and for the char the weight change in the reactor, cyclone, and hot filter vessel. The gas yields were calculated from the gas flow rate and the gas composition.

The overall mass balances were over 90 % for both oak oils and the unfiltered switchgrass oil and 86 % for the filtered switchgrass oil. Since hot filtering of

Table 4.2. Yields of major components and mass balance closures during pyrolysis

sample	oil, wt%	char, wt%	gas, wt%	mass balance, wt%
oak filtered	63.5	9.9	19.1	92.4
oak unfiltered	68.1	10.7	14.0	92.8
switchgrass filtered	52.3	16.6	16.8	85.7
switchgrass unfiltered	56.3	19.3	14.5	90.1

Table 4.3. Yields of major gas components as weight % of biomass feed

sample/mass yield	H_2, wt%	CH_4, wt%	CO, wt%	CO_2, wt%	C_2H_4, wt%	CO_2:CO
oak filtered	0.076	1.7	7.6	9.3	0.52	1.2
oak unfiltered	0.032	1.0	5.6	6.9	0.47	1.2
switchgrass filtered	0.059	0.9	5.3	10.2	0.43	2.1
switchgrass unfiltered	0.026	0.7	4.3	9.0	0.38	1.9

vapors is not expected to impact char yields, the lower mass balance closure for filtered switchgrass is likely due to loss of char. Switchgrass produced relatively large quantities of light char, and some char may have escaped the cyclone. A possible source for mass losses for all runs is light vapors that may not have properly condensed in the collection system and were not analyzed by the GC.

The oil yields were lower and char yields higher for switchgrass than for oak. Hot-vapor filtering reduced oil yields and increased gas yields, which suggests cracking reactions taking place at the filter.[59] The oil yields decreased by approximately 4 percentage points and the gas yields increased by 2-5 percentage points.

The mass yields of the major gas components are given in Table 4.3. Hot-vapor filtering increased the yields of all gas phase components. In terms of the absolute yields, the increase was largest for CO and CO_2. The CO_2:CO ratios were unaffected by the filtering. Switchgrass gave higher CO_2:CO ratios than oak, presumably due to the impact of the minerals.[66]

4.3.3. OIL ANALYSIS

The ultimate, proximate, and water by Karl-Fisher titration analysis results are in Table 4.4. These analyses are of the bio-oil products as recovered from the

66 C. Di Blasi, A. Galgano, Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis, Ind Eng Chem Res 48 (2009) 3359–3369.

Table 4.4. Bio-oil ultimate and proximate analysis results on wet oil basis

Sample	C, wt%	H, wt%	N, wt%	S, wt%	O, wt%	H_2O, wt%	fixed C, wt%	ash, wt%
oak filtered	37.3 ± 4.4	6.9 ± 0.5	0.07 ± 0.16	0.049 ± 0.002	55.7	23.3 ± 0.3	9.1 ± 0.5	0.05 ± 0.08
oak unfiltered	42.2 ± 2.6	7.0 ± 0.3	0.08 ± 0.06	0.047 ± 0.002	50.7	19.3 ± 0.2	10.1 ± 0.1	0.12 ± 0.07
switchgrass filtered	38.1 ± 1.7	7.6 ± 0.3	0.57 ± 0.13	0.073 ± 0.001	53.8	29.5 ± 0.8	7.1 ± 1.4	-0.05 ± 0.16
switchgrass unfiltered	43.3 ± 1.0	7.5 ± 0.03	0.84 ± 0.08	0.083 ±0.0004	48.3	24,0 ± 0.2	10.4 ± 2.3	1.45 ± 0.10

Table 4.5. Oil organic oxygen contents and oil carbon yields

Sample	organic O content	oil carbon yield
oak filtered	35.0	47.8
oak unfiltered	33.6	58.0
switchgrass filtered	27.5	46.1
switchgrass unfiltered	27.0	56.4

reactor system, including the dissolved water. Hot-vapor filtering decreased the ash contents, which were below detection limits for both of the filtered oils. Filtering also increased the water and O contents and decreased the C contents in the oils. The fixed carbon, which is a measure of heavy non-volatile compounds in the oils, was decreased by filtering. The organic O contents in the bio-oils were calculated from the difference in total O (determined by difference) and O in water and are shown in Table 4.5 together with oil C yields. The C yields in the bio-oil products decreased by approximately ten percentage points through hot-vapor filtering.

The contents of selected metals (Na, K, and Ca) in the oils were also measured (by atomic absorption) and are shown in Table 4.6. The metals contents were reduced significantly by hot-vapor filtering. The only exception was Na for oak, for which the Na contents were similar. It is possible that this level of Na represents background due to, for example, contamination by glass lines in the sampling system. Hot-vapor filtering reduced Ca and K contents in switchgrass bio-oil by 98 % and Na content by 76 %. The lower efficiency for Na may be due to the aforementioned Na contamination. For oak, the measured reductions were lower: 67 and 33 % for Ca and K, respectively, but the net result was a lower level of metal contamination compared to the hot-vapor filtered switchgrass bio-oil.

Table 4.6. Composition of selected metals in pyrolysis oils

Sample	Ca, µg/g	K, µg/g	Na, µg/g
oak filtered	2	6	6
oak unfiltered	6	9	5
switchgrass filtered	14	12	6
switchgrass unfiltered	683	545	25

Table 4.7. Carboxylic acid, phenolics, and carbonyl contents

sample	acids	TAN (acids)	phenolics	carbonyl
	mol/kg	mg KOH/ g	mol/kg	mol/kg
oak filtered	0.97	54.3	0.69	4.26
oak unfiltered	1.23	68.9	1.31	5.17
switchgrass filtered	1.10	61.6	0.61	4.15
switchgrass unfiltered	1.10	61.6	0.58	3.42

Table 4.8. Catalyst beds used in hydroprocessing

	components	source	particle size	total mass	total bed volume	isothermal zone
stage 1	7.8% Ru on carbon	PNNL fabricated	30-60 mesh	13.38 g	32 ml	24 ml
stage 2	3% Co & 9% Mo on Al_2O_3	Alfa-Aesar	30-60 mesh	19.62 g	32 ml	24 ml

The acid, phenolics, and carbonyl contents are shown in Table 4.7. Hot-vapor filtering reduced the contents of all of these compound classes in oak oils but increased carbonyls and did not impact acids or phenolics in hot-vapor filtered switchgrass oil.

4.3.4. HYDROPROCESSING RESULTS

The hydroprocessing tests showed good results using a two-stage catalytic hydropro-cessing strategy. Equal-sized catalyst beds, a sulfided Ru on C catalyst bed operated at 220 °C and a sulfided CoMo on Al_2O_3 catalyst bed operated at 400 °C, were used with the entire reactor at 10 MPa operating pressure. The space velocity in these tests was low; 0.2 L bio-oil (L catalyst bed)$^{-1}$ h^{-1}, for each bed or a total LHSV of 0.1 for the total treatment. The hydrogen flow was in great excess, as is typical for hydrotreating. The details are given in Table 4.8.

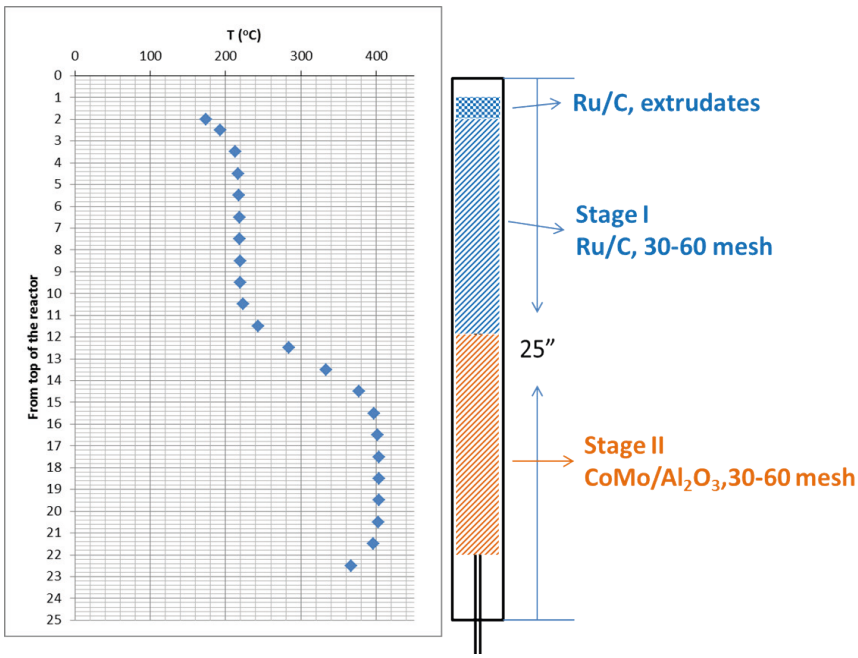


Figure 4.3. Schematic of the catalyst bed in the mini-hydrotreater reactor

Both catalyst beds were sulfided *in situ*. The reactor tube containing the catalysts was heated to 150 °C in H_2 flow, kept at 150 °C for 2 h in flow of H_2 and sulfiding agent (35 % di-tertiarybutyl-disulfide (DTBDS) in decane). Then stage 1 was heated from 150 to 250 °C in 1.2 h and held at 250 °C for 5.8 h, while stage 2 was heated from 150 to 400 °C in 3 h and held at 400 °C for 4 h with H_2 and sulfiding agent flowing. The operating pressure was 10 MPa and the sulfiding agent LHSV was 0.12 L (L cat)$^{-1}$ h^{-1}.

For the hydroprocessing tests the flow ratio of H_2/liquid was 1.89 L H_2 (L bio-oil)$^{-1}$. DTBDS was added to the bio-oil at an amount equal to 150 ppm S. The operating pressure was 10 MPa (1520 psi). These tests were kept on stream for 60 h (TOS), taking samples every 6 h. The tests were terminated as planned. Figure 4.3 shows a schematic of the catalysts beds with a super-imposed temperature profile. The temperatures were measured at the center line of the catalyst bed by a thermocouple which was adjustable within a full length thermowell. The isothermal portions of the catalyst bed are clearly shown and the lengths of the isothermal portions of the catalyst were used to calculate the space velocity.

Table 4.9. Analysis of bio-oil feedstocks used for hydroprocessing tests

sample name	C	H	H/C ratio	O	moisture	N	S	density	TAN	viscosity
	Wt% dry	Wt% dry	dry basis	Wt% dry	Wt%	Wt% wet	Wt% wet	g/ml @40°C	mg KOH/g	mm²/s @40°C
oak hot filtered	55.8	6.26	1.33	37.8	24.3	0.11	<0.005	1.215	110	28
oak non-filtered	54.9	6.28	1.36	38.7	20.3	0.07	<0.005	1.243	110	57
switchgrass hot filtered	55.8	6.28	1.34	37.2	30.7	0.79	0.03	1.164	102	19
switchgrass non-filtered	60.9	5.73	1.12	32.3	37.6	1.07	0.03	1.158	98	9.0

Table 4.10. Trace analysis of bio-oil feedstocks used for hydroprocessing tests

sample name	ICP analysis result (in ppm, wt/wt)								
	Al	Ca	Fe	K	Mg	Na	P	Si	S
oak hot filtered	<5.0	<5.0	<5.0	9.2	<5.0	18.6	<5.0	18.6	18.8
oak non-filtered	10.4	<5.0	<5.0	11.4	<5.0	20.5	<5.0	10.5	20.2
switchgrass hot filtered	<5.0	<5.0	<5.0	13.0	<5.0	17.3	<5.0	8.5	178
switchgrass non-filtered	12.8	330	11.1	535	141	40.2	68.9	182	199

The bio-oil feedstocks were analyzed at PNNL with the results shown in Table 4.9. The wet bio-oils were the samples which were actually analyzed while the reported C, H, O compositions are calculated to a dry basis by subtracting out the amount of oxygen and hydrogen in the measured moisture content. Detailed trace element analysis of the wet bio-oils was performed by ICP as shown in Table 4.10. These results for the most part confirm the earlier analyses of the products as produced at NREL and underscore the fact that bio-oil can be sampled and analyzed consistently given appropriate handling measures (cold storage and effective mixing before sampling). There is excellent agreement between the water contents measured at the two laboratories for three of the oils but the water measured for unfiltered switchgrass was higher at PNNL than at NREL. It was possible that this oil had aged during transport due to its high mineral content. After arrival at PNNL, the oil had approximately five percent undissolved solids, which also points to ageing. The acids and phenolics were measured separately at NREL, and the TAN determined at PNNL corresponded rather to the sum of both acids and phenolics.

The process results for hydrotreating the four feedstocks, as shown in Tables 4.11 to 4.14, did not vary widely. The results calculations are based on

Table 4.11. Process results over time on stream with hot-vapor filtered oak bio-oil

TOS	upgraded oil yield	oil yield, carbon basis	upgraded oil density	gas yield	produced water yield	H_2 consumed	mass balance	carbon balance
	g dry per g dry bio-oil feed	g C per g C in feed	g/ml	g gas per g dry feed	g produced water per g dry bio-oil feed	g H_2 per g dry bio-oil feed	%	%
24-30 h	0.34	0.53	0.824	0.18	0.32	0.051	85	70
36-42 h	0.39	0.61	0.845	0.19	0.34	0.048	91	78
48-54 h	0.49	0.76	0.853	0.19	0.35	0.049	99	93

Table 4.12. Process results over time on stream with unfiltered oak bio-oil

TOS	Upgraded Oil Yield	Oil Yield, Carbon basis	Upgraded Oil density	Gas yield	Produced water yield	H_2 consumed	Mass Balance	Carbon Balance
	g dry per g dry bio-oil feed	g C per g C in feed	g/ml	g gas per g dry feed	g produced water per g dry bio-oil feed	g H_2 per g dry bio-oil feed	%	%
24-30 h	0.42	0.66	0.843	0.15	0.30	0.045	87	80
36-42 h	0.44	0.70	0.854	0.18	0.35	0.047	94	85
48-54 h	0.41	0.66	0.863	0.19	0.33	0.047	91	81

Table 4.13. Process results over time on stream with hot-vapor filtered switchgrass bio-oil

TOS	Upgraded Oil Yield	Oil Yield, Carbon basis	Upgraded Oil density	Gas yield	Produced water yield	H_2 consumed	Mass Balance	Carbon Balance
	g dry per g dry bio-oil feed	g C per g C in feed	g/ml	g gas per g dry feed	g produced water per g dry bio-oil feed	g H_2 per g dry bio-oil feed	%	%
24-30 h	0.44	0.67	0.813	0.18	0.37	0.047	96	90
36-42 h	0.47	0.73	0.819	0.18	0.38	0.046	99	95
48-54 h	0.50	0.77	0.832	0.19	0.44	0.047	105	100

the bio-oil feedstock for the hydrotreating test. Mass balances for oak runs ranged from 85 to 99 % for the steady-state windows calculated, with carbon balances somewhat lower, ranging from 70 to 93 %. The data for the hot-vapor filtered switchgrass runs was somewhat better with mass balances ranging from 93 to 105 % and carbon balances from 90 to 100 %. For the unfiltered

Table 4.14. Process results over time on stream with unfiltered switchgrass bio-oil

TOS	Upgraded Oil Yield	Oil Yield, Carbon basis	Upgraded Oil density	Gas yield	Produced water yield	H_2 consumed	Mass Balance	Carbon Balance
	g dry per g dry bio-oil feed	g C per g C in feed	g/ml	g/g dry feed	g/g dry feed	g/g dry feed	%	%
24-30 h	0.40	0.56	0.802	0.19	0.35	0.048	93	76
36-42 h	0.42	0.60	0.832	0.19	0.33	0.048	94	79
48-54 h	0.44	0.61	0.830	0.19	0.33	0.051	94	80

bio-oil the carbon balances were only 76 to 80 %. On a mass balance adjusted basis the carbon balances ranged from 82 to 94 for oak and from 94 to 97 % for hot-vapor filtered switchgrass but only 82 to 85 % for the unfiltered bio-oil. Since the liquid and gaseous products were all measured, the carbon loss can be attributed to experimental error and to deposits on the catalyst particles. A typical catalyst bed following an experimental run had evidence of carbonaceous deposits in the range of the top of heat-up zone for each catalyst, as shown in Figure 4.4. The balance of the catalyst beds were free flowing and easily removed from the reactor tube for analysis.

The hot-filtered oak bio-oil performed nearly flawlessly for 60 h while the non-filtered version seemed to work almost as well, but with a bit larger portion of slightly fouled bed (but still no pressure drop). The hot-filtered switchgrass bio-oil also appeared to work nearly flawlessly. However, the unfiltered switchgrass bio-oil had ~5 wt% undissolved solids, which separated out in the pump and were not processed. Even with these solids not processed, there was still a pressure drop build-up after 50 h. It is hypothesized that solids in the unfiltered bio-oil led to plugging in the packed catalyst bed, causing the pressure drop.

The products from the four tests were similar. The light oil phase product appeared fully hydrotreated. The density of the products varied from 0.82 g/mL up to 0.85 g/mL over the period of the test with a correlated change of the hydrogen to carbon atomic ratio from 1.8 down to 1.6. In Table 4.9 there are two hydrotreated bio-oil products for each test, one early on after catalyst break-in (24-30 h TOS) and one at the end of the test (48-54 h TOS). As shown in Table. 4.15 the hydrotreating was quite effective, reducing the sulfur and nitrogen below the level of detection and reducing the oxygen to a low level.

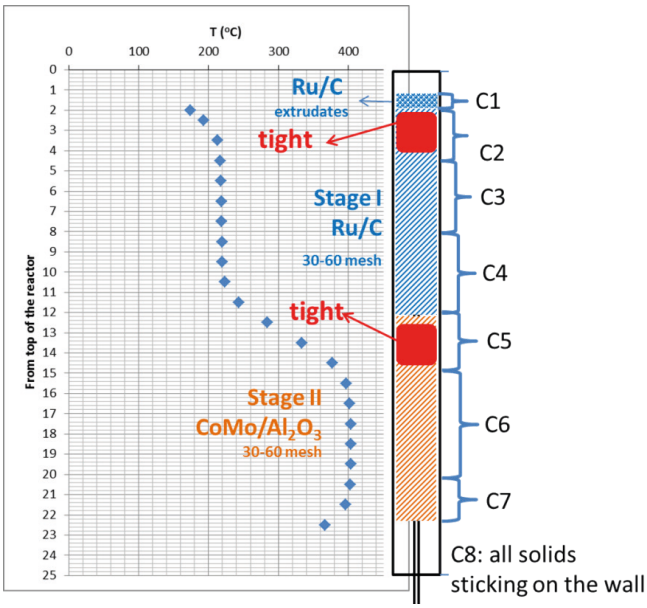


Figure 4.4. Schematic of the catalyst bed after use with unfiltered switchgrass

Table 4.15. Hydrotreated bio-oil product composition and density

TOS	C	H	H/C ratio	O	Moisture	N	S	Density
	wt% dry	wt% dry	dry basis	wt% dry	wt%	wt% wet	wt% wet	g/mL
hot-vapor filtered oak								
24-30 h	86.9	12.5	1.71	0.58	0.040	<0.05	<0.005	0.824
48-54 h	87.2	12.2	1.66	0.60	0.000	<0.05	<0.005	0.853
unfiltered oak								
24-30 h	87.3	12.2	1.66	0.50	0.000	<0.05	<0.005	0.843
48-54 h	88.1	11.7	1.57	0.26	0.000	<0.05	<0.005	0.863
hot-vapor filtered switchgrass								
24-30 h	85.5	12.5	1.74	2.0	<0.01	<0.05	<0.018	0.813
48-54 h	85.7	12.2	1.69	2.1	<0.01	0.06	<0.016	0.832
unfiltered switchgrass								
24-30 h	85.3	12.9	1.79	1.8	<0.01	<0.05	<0.018	0.802
48-54 h	85.6	12.3	1.71	2.0	<0.01	0.06	<0.014	0.830

The trend over the time on stream shows a mild deactivation of the catalytic process as the density increases as does the remaining amount of heteroatoms

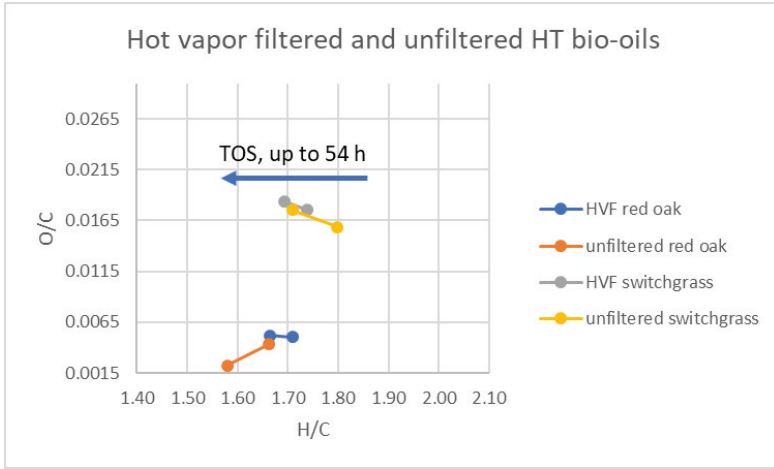


Figure 4.5. van Krevelen plot of hydrotreated products from hot vapor filtered bio-oils

in all cases. Further evidence of the reduced level of hydrogenation is the lower hydrogen to carbon atomic ratio later in each test. The effect of feedstock is notable in that the hydrotreated oak bio-oils contain less oxygen than the hydrotreated switchgrass bio-oils. The effect of higher oxygen, which typically results in an increased density, is, in this case, counter balanced by the more complete saturation of the switchgrass bio-oil such that the hydrotreated switchgrass bio-oils have higher H/C ratios and lower densities.

For the purposes of this thesis, a van Krevelen analysis has been applied to the hydrotreating products. As seen in Figure 4.5, the change in product compositions over the time of the experiment (54 h) seems to suggest catalyst deactivation although there are only two points in each analysis. The unfiltered red oak bio-oil seems to have a different result with a loss in hydrogenation activity while the deoxygenation increased.

The product gas composition was also quite consistent throughout these tests. In Table 4.16 there are two gas products for each test, one early on after catalyst break-in (24-30 h TOS) and one at the end of the test (54-60 h TOS). The composition is presented on a hydrogen-free basis and shows only the product gases. For these tests there was a large excess of hydrogen, as is typical for hydrotreating, amounting to about 95 vol % of the process off-gas. A clear trend in increasing carbon oxides and decreasing hydrocarbon products is seen from the beginning to the end of all the tests. There are small differences between the two biomass typesin that hydrotreatment of switchgrass bio-oil

Table 4.16. Product gas composition in bio-oil hydrotreating, volume percent (H_2-free basis)

TOS	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO	CO_2
hot-vapor filtered oak							
24-30 h	19.6	23.1	12.1	6.7	2.5	2.4	33.8
54-60 h	19.7	21.9	11.6	6.1	2.2	2.6	36.0
unfiltered oak							
24-30 h	19.3	25.5	12.0	3.0	2.8	2.8	34.4
54-60 h	17.8	22.0	10.7	2.6	2.1	3.4	41.4
hot-vapor filtered switchgrass							
24-30 h	15.2	32.6	24.2	8.8	3.8	1.8	13.5
54-60 h	14.1	29.6	22.7	8.4	3.5	2.4	19.3
unfiltered switchgrass							
24-30 h	12.5	29.3	25.8	5.1	4.2	2.4	20.6
54-60 h	12.5	24.4	23.3	4.9	3.8	3.4	27.8

produced less CO_2 and methane, but more of the other hydrocarbons. The single significant difference between hot-vapor filtered and unfiltered bio-oils was the amount of butane (in both feedstock cases) which was nearly double in the hot-filtered cases. There is no obvious explanation for this difference. There is also a slightly larger amount of methane and slightly lower amount of carbon dioxide in the product gas from the hot-filtered bio-oils.

The variation in the mineral content in the bio-oils and the fate of the minerals in the hydroprocessing tests were determined. In the case of the oak bio-oil, the difference in the mineral content is not great, between the HVF and the unfiltered bio-oils (see Table 4.6 and 4.10). Analysis of the catalyst bed fractions after the hydrotreating tests shows that mineral deposition is not a factor for either test. In the test with HVF oak bio-oil, the amounts of Ca, K, and Na, as well as the Al and Si, actually are lower by half in the front-end catalyst bed of Ru on C after use, suggesting that those elements are transported from the bed. Similarly, the levels in the finishing catalyst bed of sulfided CoMo on Al_2O_3 are also reduced except for the K, which is higher after the test. In the test with the unfiltered oak bio-oil the result is almost identical. The noticeable difference in the analysis of the catalyst beds was the significant increase in Fe, Ni, Cr, and Mo in both. These metals apparently are corrosion products from the reactor walls.

Also, sulfidation of the catalysts was verified wherein the sulfur content was equivalent to a 71 and 125 % molar equivalent to the Ru loading for the HVF

and the unfiltered, respectively. The sulfur molar ratio equivalent to the CoMo loading was 1.4 and 1.3. The Ru catalyst loading is consistent with a 35 and 63 % sulfidation as RuS_2, a typical level, based on literature reports suggesting similar (40 %) Ru sulfidation in a hydrothermal environment.[67] The ratio of S to metals in the CoMo catalyst suggested that the metals were 87 and 83 % of fully sulfided.

In the case of the switchgrass bio-oil, the difference in the mineral content was more significant, between the HVF and the unfiltered bio-oils (see also Table 4.6 and 10). Analysis of the catalyst bed fractions after the hydrotreating tests showed that mineral deposition was significant when processing the unfiltered bio-oil, see Table 4.17. The analysis of each catalyst prior to the tests (fresh) is given for comparison in Table 4.17. In the test with HVF switchgrass bio-oil, the amounts of Ca, and K, as well as the Al and Si, actually were lower by half in the Ru catalyst bed after use, as was seen with oak bio-oils. Also, the levels of those elements in the CoMo catalyst were reduced except for the K, which was higher after the test. In both beds, the Na was slightly elevated from the beginning level after the test.

In the hydrotreating test with the unfiltered switchgrass bio-oil, the result was noticeably different. As shown in Table 4.17, the Ca, P, and Mg were all much higher in the fouled front end of the Ru/C catalyst bed, where the fouling occurred, suggesting deposition of Ca and Mg phosphates. The Na and Si were only slightly higher than in the fresh catalyst while the K was slightly lower. Of potentially greater concern was the noticeable deposition in the catalyst bed of the corrosion products Ni, Fe, Mo, and Cr (see Table 4.17). These deposits are more noticeable in the Ru/C bed after processing the hot-vapor filtered bio-oils.

The sulfidation of the catalysts was also verified for these two tests. The S content was equivalent to 71 % and 121 % molar equivalent to the Ru loading and 1.0 and 1.3 molar ratio equivalent to the CoMo loading. The Ru catalyst loading was consistent with a 35-61 % sulfidation as RuS_2, typical in a hydrothermal environment. The ratio of S to metals in the CoMo catalyst suggested that the metals were 63-84 % of fully sulfided, slightly less than in the oak bio-oil tests.

The ruthenium analysis reports a lower level in the used catalysts. Carbon deposition in the pores of the catalyst has been determined to be the agent diluting the ruthenium concentration rather than actual leaching of the metal

67 M. Dreher, B. Johnson, A.A. Peterson, et al. Catalysis in supercritical water: Pathway of the methanation reaction and sulfur poisoning over a Ru/C catalyst during the reforming of biomolecules. Jour Catal 301 (2013) 38-45.

Table 4.17. Catalyst analyses for switchgrass bio-oil hydroprocessing, in ppm

	Ru on carbon extrudate catalyst					sulfided CoMo on alumina catalyst			
	fresh	HVF		unfiltered		HVF		unfiltered	fresh
		fouled	free	fouled	free	half fouled	free	free	
Al	695	125	252	289	364	324500	346450	335700	41400
Ca	417	94	90	13660	170	812	817	1268	1098
Co	<40	<25	<25	<25	<25	28555	31115	30010	35220
Cr	<40	24	151	71	253	6334	378	1887	<40
Fe	199	3526	1176	822	1639	18670	1688	5528	107
K	443	128	111	290	274	191	64	5192	80
Mg	281	<25	<25	561	162	581	498	1183	578
Na	74	99	96	116	107	302	286	514	246
Ni	<40	3268	295	2602	66	542	615	845	543
P	<40	<25	<25	4114	<25	9584	10550	10135	9606
Mo	<40	130	90	237	42	58505	62985	61205	76485
Si	1026	210	450	1347	721	1246	1325	1316	1793
S	3145	9544	9723	12815	11605	38270	37250	47695	1228
Ru	51970	39630	44268	39470	45490	<25	<25	<25	<25
C	NA	NA	NA	NA	NA	109600	111600	104200	<500
N	NA	NA	NA	NA	NA	6700	6200	11200	500

from the support. This effect is confirmed with the CoMo catalyst wherein the carbon deposition can be quantified by direct elemental analysis. The carbon deposition is fairly uniform through the bed suggesting that it is not related to the fouling of the catalyst bed. It appears that Fe and Cr deposition correlate most directly with fouling of the CoMo catalyst bed.

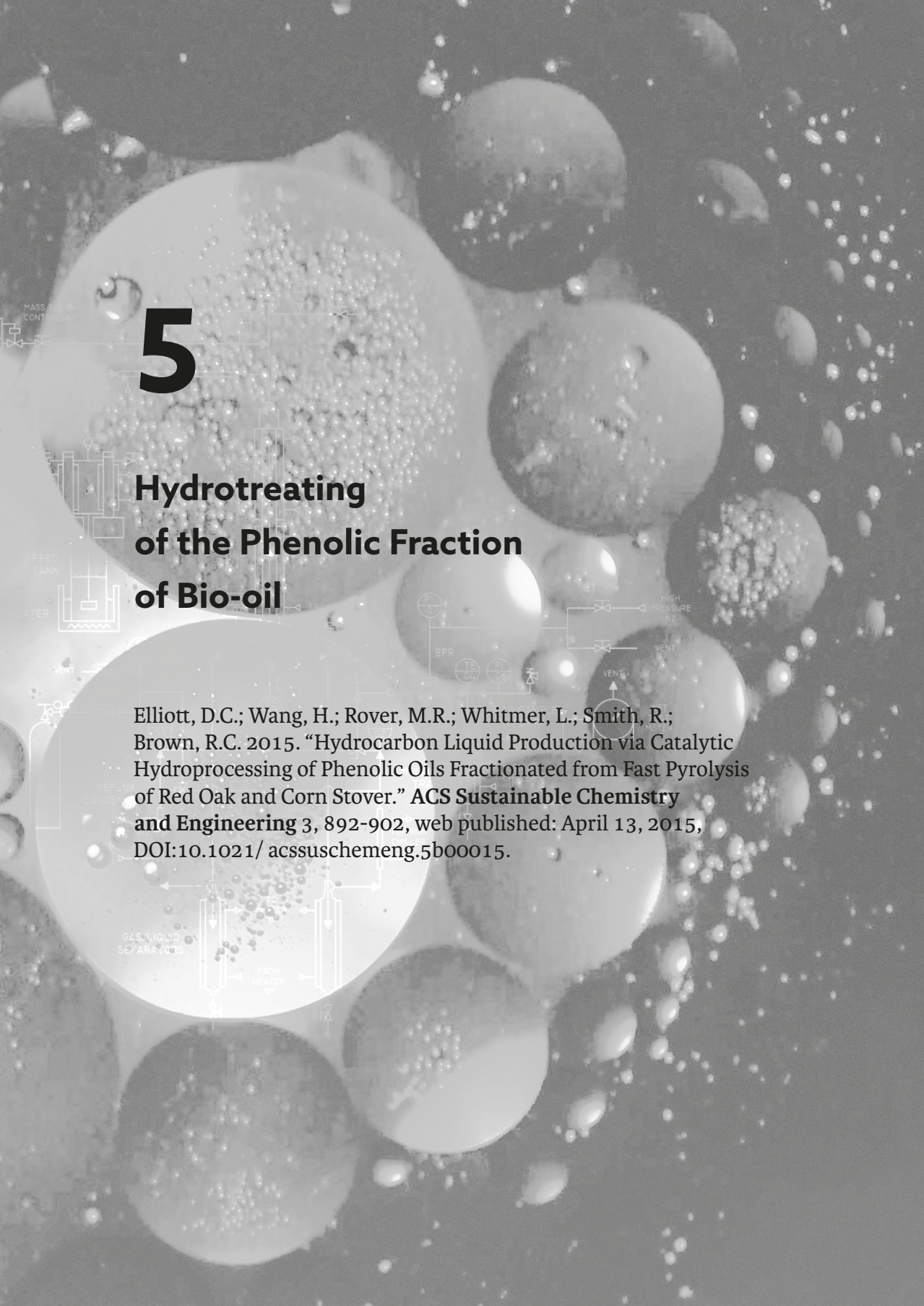
4.4. CONCLUSIONS

One-liter samples of four fast pyrolysis bio-oils were produced with oak and switchgrass feeds, both with and without the hot-vapor filter. In the runs without the hot-vapor filter, the filter element was removed, but the empty housing remained in place, so the residence time at temperature remained constant.

The analysis of the results showed the following:

- Hot-vapor filtering reduced bio-oil yields and increased gas yields (see Table 4.2). The yields of fuel carbon as bio-oil were reduced by ten percentage points by hot-vapor filtering for both feedstocks (see Table 4.5).

- The ash and metal contents were reduced by the hot-vapor filtering (see Table 4.6). The K and Ca contents were reduced by 98 % for switchgrass and somewhat less for oak, which was much lower in mineral content even without HVF.
- The H_2O and O contents were higher and C contents were lower in the hot-vapor filtered bio-oils than the unfiltered (see Table 4.4).
- Hot-vapor filtering reduced the contents of acids, phenolics, and carbonyls in oak oils but increased carbonyl content in hot-vapor filtered switchgrass oil while the phenolics and acids were essentially unchanged (see Table 4.7).
- The hydroprocessing products from the four tests were similar. There was nearly complete heteroatom removal by the hydrotreating, with O reduced to <0.6 % for the oak and <2 % for the switchgrass while N and S were reduced to <0.05 %.
- The hydrotreatment of the hot-vapor filtered bio-oils, which were low in mineral content even unfiltered, showed minimal differences in catalyst activity over a 5-day test, but the elemental analysis of the used catalyst beds showed evidence of less deposition compared to the catalysts used with non-filtered bio-oils.



5

Hydrotreating of the Phenolic Fraction of Bio-oil

Elliott, D.C.; Wang, H.; Rover, M.R.; Whitmer, L.; Smith, R.; Brown, R.C. 2015. "Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover." **ACS Sustainable Chemistry and Engineering** 3, 892-902, web published: April 13, 2015, DOI:10.1021/ acssuschemeng.5b00015.

5.1. INTRODUCTION

Fast pyrolysis of biomass is widely held to be a viable technology for the direct production of liquid fuels.[68] The bio-oil product from such processes, however, is not considered of sufficient quality for direct use as petroleum refinery feedstock. Bio-oil fuel properties can be improved considerably via catalytic hydrotreatment and catalytic cracking.[69] Hence, catalytic hydroprocessing has been developed to convert the highly oxygenated bio-oil components into hydrocarbon liquids.[70] Much of the recent work in bio-oil hydrotreating has been performed using precious metal catalysts[71] in small batch reactors for short periods of time.[72] In contrast the work reported here is performed in continuous-flow reactor configuration with a pre-sulfided catalyst that is resistant to sulfur poisoning and has been operated for days and weeks on stream.[73] Lindfors et al.[69] used fractionation of bio-oil prior to upgrading as a more efficient way of producing liquid fuels versus treating the whole bio-oil. Due to the mixture of different functional groups in whole bio-oil, problems are created because these functional groups react under specific conditions utilizing different catalysts.[69,70] Sugar-type compounds are known to be susceptible to coking and the removal of this fraction prior to upgrading protocols would be advantageous.[69] In comparison to the water soluble phase of bio-oil the water insoluble phase is more difficult to upgrade because of high molecular weight aromatic structures derived from pyrolysis of the biomass lignin fraction.[74] Effective bio-oil fractionation prior to upgrading may be a valuable approach of producing liquid fuels and chemicals versus upgrading whole bio-oil.[69,75]

68 A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading. Biomass & Bioenergy 38 (2012) 68–94.

69 C. Lindfors, E. Kuoppala, A. Oasmaa, Y. Solantausta, V. Arpiainen, Fractionation of bio-oil. *Energy Fuels* **2014** *28* (5785).

70 Elliott, D. C. Historical developments in hydroprocessing bio-oils. Energy & Fuels 21 (2007) 1792-1815.

71 H.Wang, J. Male, Y. Wang, Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. ACS Catal 3 (2013) 1047-1070.

72 F.dM. Mercader, P.J.J. Koehorst, H.J. Heeres, S.R.A. Kersten, J.A. Hogendoorn, Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. AIChE Jour 57(11) (2011) 3160-3170); A.R. Ardiyanti, S.A. Khromova, R.H. Venderbosch, V.A. Yakovlev, I.V. Melián-Cabrera, H.J. Heeres, Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. Appl Catal A: General 449 (2012) 121-130.

73 A.H. Zacher, M.V. Olarte, D.M. Santosa, D.C. Elliott, S.B. Jones, A review and perspective of recent bio-oil hydrotreating research. Green Chem 16 (2014) 491-516.

74 H. Ben, W. Mu, Y. Deng, A.J. Ragauskas, Production of renewable gasoline from aqueous phase hydrogenation of lignin pyrolysis oil. *Fuel 103* (2013) 1148.

75 F.dM. Mercader, M.J. Groeneveld, S.R.A. Kersten, C. Geantet, G. Toussaint, N.W.J. Way, et al. Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. Energy Environ Sci 4 (2011) 985.

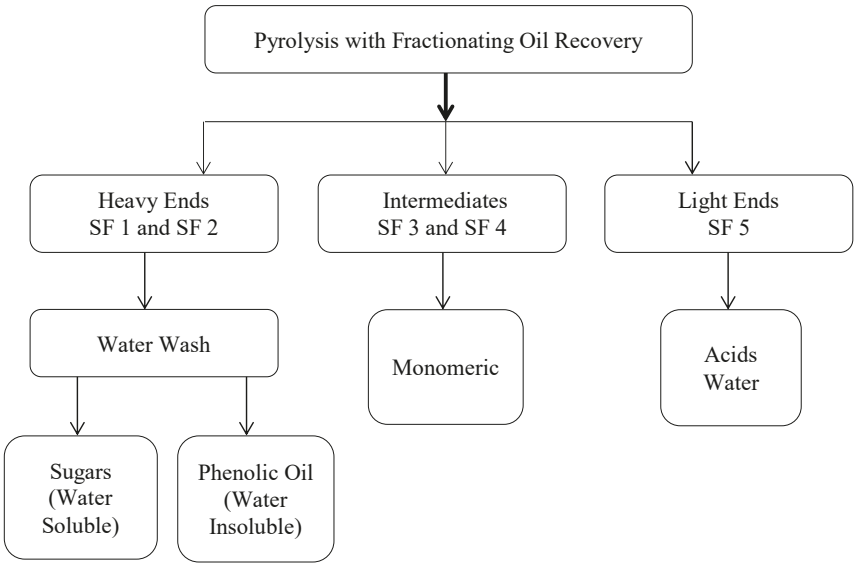


Figure 5.1. Procedure for the recovery of phenolic compounds from Iowa State University's bio-oil fractionating recovery system. [76,77]

Iowa State University has developed a fractionating bio-oil recovery system that allows for collection of bio-oil as heavy-ends (stage fraction (SF) 1 and SF 2), intermediate fractions (SF 3 and SF 4), consisting of monomeric compounds, and light ends (SF 5) that contain the majority of acids and water (Figure 5.1).[76,77] Complete details on the reactor and recovery system can be found in Pollard et al.[76] and Rover et al.[77] The mass distribution (wet basis) when using red oak feedstock is approximately 40-45 wt% for SF 1 and SF 2 heavy ends, 10 wt% for SF 3 and SF 4 intermediates, and 45-50 wt % of SF 5 light ends. The principle of the heavy ends is to collect high boiling point phenolic oligomers derived from lignin and anhydrosugars, such as levoglucosan, derived from cellulose and hemicellulose. The purpose of the intermediate fractions is to collect monomeric compounds with condensation points near phenol. Whereas, the light ends collect approximately 60-70 wt% moisture, 8-12 wt% acids (i.e. acetic, formic, glycolic, propionic) and 20-30 wt% other light oxygenates.

76 Pollard, A. S.; Rover, M. R.; Brown, R. C. Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties. *Jour. Anal. Appl. Pyrol* **2012**, *93*, (129-138).

77 Rover, M. R.; Johnston, P. A.; Whitmer, L. E.; Smith, R. G.; Brown, R. C. The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions. *Jour. Anal. Appl. Pyrol.* **2014**, *105*, (262-268).

The objective of this research was to evaluate the potential production of petroleum refinery feedstocks derived from biomass via fast pyrolysis and product fractionation. In this case, fractionation of the bio-oil and washing of the heavy ends (SF 1 and SF 2) resulted in a phenolic oil product which served as the feedstock for hydroprocessing to a more hydrocarbon-like refinery feedstock. To date, the vast majority of research in hydrotreating bio-oil to produce liquid transportation fuels is centered upon stabilizing bio-oils through chemical means, including condensed phase low-temperature hydroprocessing[78,79] or vapor phase treatment, such as catalytic pyrolysis.[80] This study was formulated to assess the impact of the bio-oil fractionation and to determine if existing barriers, particularly hydrotreating catalyst lifetime, can be mitigated through the use of bio-oil fractions to form a more stable hydroprocessing feedstock.

Woody and herbaceous biomass were selected as the feedstocks for this study. Bio-oil fractions were produced in a fluidized-bed reactor at Iowa State University (ISU). Pacific Northwest National Laboratory (PNNL) hydrotreated the phenolic oils recovered from the bio-oil in a bench-scale, continuous-flow, packed bed catalytic reactor to assess the prospects for subsequent hydroprocessing to hydrocarbon fuels. This collaboration between ISU and PNNL leverages existing expertise to assess the impact of bio-oil fractionation at ISU[76,77] on the hydrotreating process to produce liquid transportation fuels at PNNL.[81]

5.2. EXPERIMENTAL

5.2.1. FEEDSTOCKS

Pre-dried red oak (*Quercus rubra*) chips were obtained from Wood Residual Solutions, LLC of Montecello, WI with a moisture content of approximately 10 %. Corn stover feedstock (comprised of leaves, stalks, and cobs) was obtained locally through ISU's Agricultural and Biosystems Engineering

78 Wildschut, J.; Mahfud, F. H.; Venderbosch, R. H.; Heeres, H. J. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Ind. Eng. Chem. Res.* **2009** *48* (10324-10334).

79 Oasmaa, A.; Elliott, D. C. Process for stabilizing fast pyrolysis oil and stabilized fast pyrolysis oil. patent application US 2012/0285079 A1 2012.

80 Mihalcik, D. J.; Mullen, C. A.; Boateng, A. A. Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. *J. Anal. Appl. Pyrol.* **2011**, *92*, (224-232).

81 Elliott, D. C.; Hart, T. R.; Neuenschwander, G. G.; Rotness, L. J.; Olarte, M. V.; Zacher, A. H.; Solantausta, Y. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. *Energy Fuels* **2012**, *26*, (3891-3896).

Department and was harvested using traditional multi-pass harvesting techniques. The stover was dried using a permeable floor semitrailer peanut drier to a nominal moisture content of 10 %. Both feedstocks were then milled to size using an Artsway, 60hp hammer mill equipped with a 3mm screen.

The amounts of biomass fed, bio-oil, and char were measured gravimetrically over a steady-state collection period as weight changes of collection vessels at appropriate points in the system. For the biomass, this was mass loss in the Acrison feeder; for the bio-oil, the sum of the weight changes in the liquid collection bottles as it exited the condensation train; and for the char, the weight change of the reactor bed material and cyclone char catches. The gas yields were calculated by injecting a known amount of helium into the front end of the system using a calibrated mass flow controller and measuring gaseous concentration, as they exited the system, using a Varian CP-4900 micro-GC.

5.2.2. FAST PYROLYSIS AND FRACTIONATION

The feedstocks were pyrolyzed at 500°C. The red oak biomass feed rate was 4.8 kg/h with 114 SLPM nitrogen flow, whereas, the corn stover biomass feed rate was 5.7 kg/h with 183 SLPM nitrogen flow, utilizing a fluidized bed reactor with a staged bio-oil recovery system (Figure 5.2). Stage 1, a condenser, collects high boiling point constituents such as anhydrosugars and phenolic oligomers. The temperature was controlled using a shell-and-tube heat exchanger with gas inlet and outlet temperatures of 345 °C and 102 °C, respectively. Stage 2, an electrostatic precipitator, collects aerosols and was operated at 40 kV DC and heat traced to 125 °C to prevent vapor condensation. The noncondensable gases were quantified utilizing a micro-GC with a He gas internal standard. This condensation system allows for the collection of lignin-derived phenolics in stage fraction (SF) 1 and SF 2 providing a stream of heavy-ends from the bio-oil that can be processed further.

During the production of bio-oil, SF 1 and SF 2 were combined and subjected to water washing to separate the water-soluble, carbohydrate-derived components from the water-insoluble phenolic oil (Figure 5.1).[70,71] SF 1 and SF 2 were together mixed with deionized water in a 1:1 ratio by weight. The resulting solution was mixed thoroughly to blend the stage fractions and water. The samples were placed on a shaker table (MaxQ 2506, Thermo Scientific, Hanover Park, IL) for 30 min at 250 motions/min and centrifuged (accuSpin1R, Thermo Scientific, Hanover Park, IL) at 2561 g force for 30 min. The water soluble portion (sugar-rich solution) was decanted from the phenolic oil and

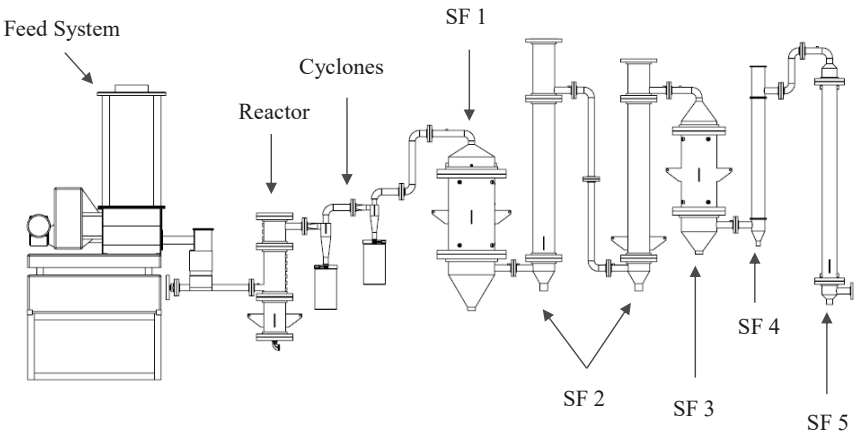


Figure 5.2. Process diagram for fluidized-bed reactor with fractionating condensation system.

rotary evaporated at 40 °C to remove the water. Complete details can be found in Rover et al.[82]

5.2.3. HYDROPROCESSING

The phenolic oil samples produced at ISU from red oak wood and corn stover were shipped to PNNL. The phenolic oils were hydroprocessed in the mini-hydrotreater (Figure 5.3). In fact, the precious metal (non-sulfided) tests were performed in a different, but similar, reactor system than were the sulfided CoMo tests. In all cases the hydrotreater was configured as a single pass, co-current, continuous, down-flow reactor. The system can operate at up to 12.4 MPa (1800 psig) with a maximum catalyst temperature 400 °C. It is described in detail by Elliott et al.[83]

The mini-scale hydrotreaters (30 mL fixed bed) were built for bio-oil upgrading by catalytic hydroprocessing. Tests with the red oak phenolic oil were completed with either sulfided or non-sulfided catalysts as shown in Table 5.1.

Campaigns were performed for each feed over the course of a five-day test, and the products and feed were collected to assess performance for each phenolic oil feed type with the two catalyst systems to compare to the results with conventional whole (unfractionated) bio-oil. For all of the reported tests,

82 Rover, M. R.; Johnston, P. A.; Jin, T.; Smith, R. G.; Brown, R. C.; Jarboe, L. Production of Clean Pyrolytic Sugars for Fermentation. *Chem. Sus. Chem.* **2014** *7* (1662).

83 Elliott, D. C.; Wang, H.; French, R.; Deutch, S.; Iisa, K. Hydrocarbon liquid production from biomass via hot-vapor filtered fast pyrolysis and catalytic hydroprocessing of the bio-oil. *Energy Fuels*, **2014**, *28*, (5909-5917).

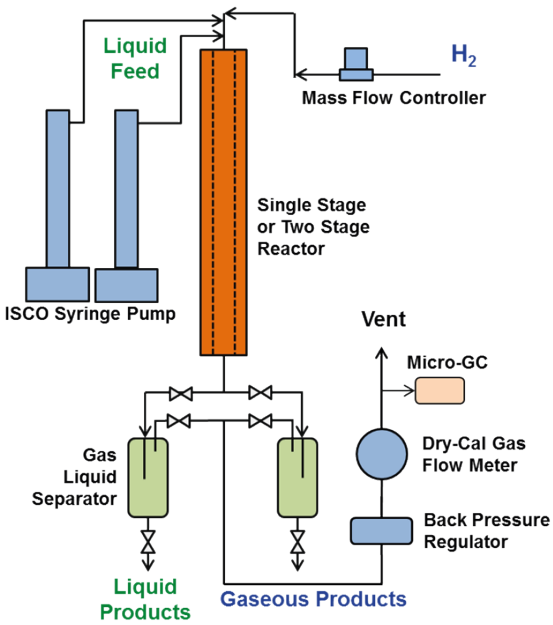


Figure 5.3. Schematic of the mini-reactor hydrotreater system

Table 5.1. Summary of hydrotreater tests with red oak phenolic oil

temperature	pressure	LHSV	catalyst	TOS	comment
350 °C	10.5 MPa	0.5	5%Pd-5%Re*	6 h	plug
140 °C / 370 °C	12.1 MPa	0.2/0.2	7.8%Ru*/2.5%Pd*	24 h	feed line plugged
140 °C / 370 °C	12.1 MPa	0.1/0.1	7.8%Ru*/2.5%Pd*	48 h	catalyst bed clear
400 °C	10.4 MPa	0.5	CoMo oxides presulfided**	5 h	catalyst bed fouled
400 °C	12.5 MPa	0.2	CoMo oxides presulfided**	18 h	catalyst bed fouled

* PNNL fabricated on granular carbon, 30-60 mesh**Alfa Aesar #40435, 3.5% CoO, 14%MoO_3 on alumina, ground to 30-60 mesh

the products and data were collected over the entire period with individual products and data sets collected in operating windows from 2 to 6 h long. The hydrogen consumption has been calculated and the yield of gas and oil products determined.

For the CoMo tests, the catalyst bed was sulfided *in situ*. The reactor tube containing the catalyst was heated to 150 °C in H_2 flow, heated from 150 °C to 350 °C over 3 h in flow of H_2 and sulfiding agent (35 % di-tertiarybutyl-disulfide

(DTBDS) in decane), and then heated to 400 °C and held for 5 h with H_2 and sulfiding agent flowing.

For the hydroprocessing tests the flow ratio of H_2/liquid was 2500 L H_2 (L bio-oil)$^{-1}$. The operating pressure was typically 12 MPa (1780 psi). Hydrogen consumption was calculated by difference between hydrogen fed to the reactor and the hydrogen recovered in the gas product. When using the sulfided catalyst, DTBDS was added to the phenolic oil at an amount equal to 150 ppm S. Figure 5.4 shows a schematic of the catalyst beds with a super-imposed temperature profile for the single stage and the two-stage testing modes. The temperatures were measured at the center line of the catalyst bed by a thermocouple, which was adjustable within a full length thermowell. The isothermal portions of the catalyst bed are clearly shown and the lengths of the isothermal portions of the catalyst were used to calculate the space velocity. The liquid hourly space velocity used in these studies was liters of phenolic oil feed per liter of catalyst bed per hour.

5.2.4. ANALYTICAL METHODS

Moisture content of the heavy ends from SF 1 and SF 2 were determined by titration using Karl Fisher described in literature.[84] The water-insoluble content (often used as an estimation for amount of phenolic monomer/oligomers) was determined by an 80:1 water-to- bio-oil ratio and described by Pollard et al.[76] The ultimate analysis of the phenolic oil and feedstocks weredetermined utilizing Elementar, vario MICRO cube (Elementar, Hanau, Germany) elemental analyzer, with oxygen determination by difference. A minimum of three trials was performed with standard deviation calculated.

The phenolic oils and hydrotreated products were characterized at PNNL for elemental analysis including C, H, N (ASTM D5291), O (ASTM D5373), and S (ASTM D1552), Total Acid Number (TAN, ASTM D3339), water content (ASTM D6869), metals content (ICP-OES, QC standards tested before and after the unknowns), and filterable solids for the phenolic oils were determined using ASTM D7579. Viscosity and density were determined with the Stabinger apparatus using ASTM D7042. In addition, the products were analyzed by simulated distillation (ASTM D2887) in order to assess the relative amounts of fuel products in the gasoline, diesel, jet fuel, heavy oil, and residual ranges. Semi-quantitative analysis of the two phenolic oils was performed with gas

84 Rover, M. R.; Johnston, P. A.; Lamsal, B. P.; Brown, R. C. Total water-soluble sugars quantification in bio-oil using the phenol–sulfuric acid assay. *Jour. Anal. Appl. Pyrol.* **2013**,*104*,(194-201).

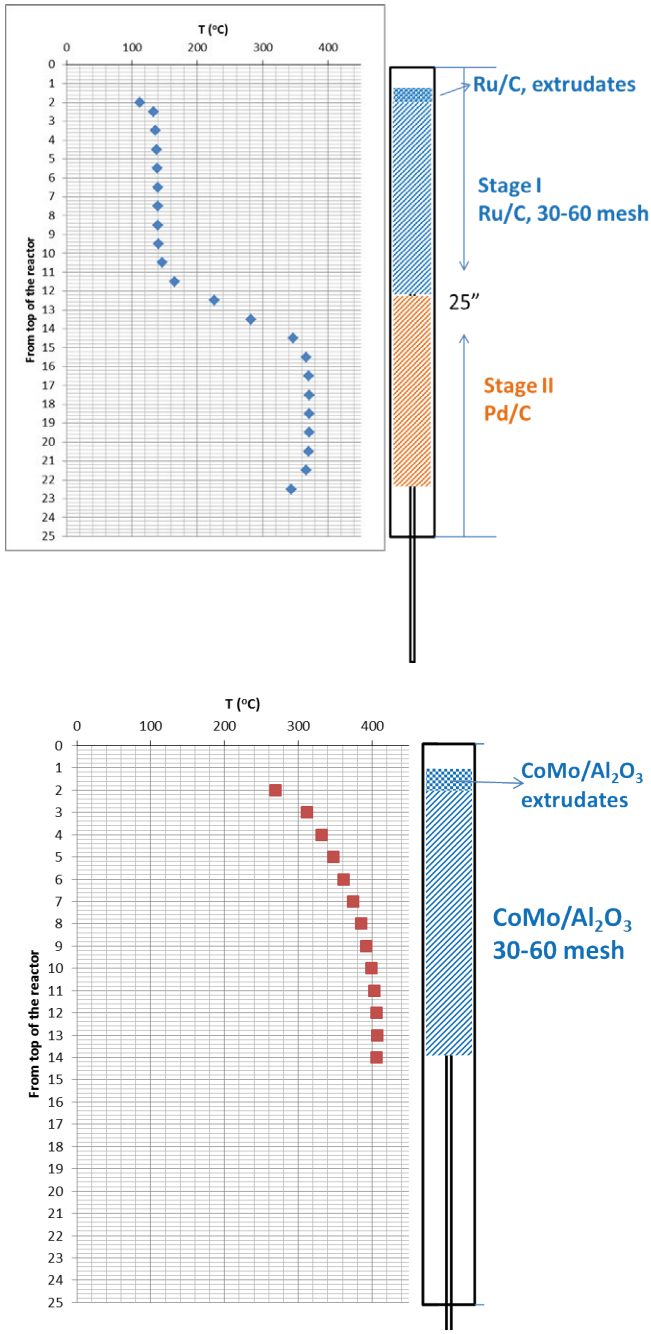


Figure 5.4. Schematic of the catalyst beds in the mini-hydrotreater reactor

chromatography-mass spectrometry (GC-MS). Using a DB-5 column over a temperature program separation of the phenolic oils was performed and mass spectrometric analysis undertaken with a Mass Selective Detector. Using the Agilent peak matching program, tentative identifications were applied to the components and their relative quantities determined based on total ion current.

5.2. RESULTS

5.2.1. FEEDSTOCKS

Results from the analyses of the feedstocks as fed to the fast pyrolysis system are shown in Table 5.2. The main difference between the feedstocks is the ash, which was twenty times higher in corn stover than in oak.

Table 5.2. Composition of biomass feedstocks

	proximate analysis (wt %)			ultimate analysis (wt %)					
sample	moisture	volatiles	fixed carbon	ash	C	H	N	S	O (by diff)
red oak	6.1	79.7	13.8	0.39	49.6	6.03	0.08	0.01	43.9
corn stover	6.0	81.5	10.4	8.06	43.2	6.33	0.90	0.15	41.4

5.2.2. FAST PYROLYSIS AND FRACTIONATION RESULTS

The yields of the major components (bio-oil, char, and gas) in the fast pyrolysis experiments are shown in Table 5.3. The high overall mass balances for both oak and corn stover suggest good operations. The yields of the three major classes of bio-oil fractions are also given in Table 5.3. The heavy ends fractions were separated offline into sugar solution (water soluble) and phenolic oil (water insoluble) streams using the water wash technique described in the methods section. Rover et al.[81] reported that the water soluble and partially soluble constituents in red oak bio-oil that were carried into the sugars stream were 6.5 wt% constituents other than sugars for SF 1 and 3.2 wt% for SF 2. On a biomass basis, the mass yields (wet basis) of fractionated products from the red oak were 10.7 wt% water insoluble phenolic oil with 18.0 wt% water soluble constituents. The mass yields (biomass basis wet basis) of fractionated products from the corn stover were 9.00 wt% water insoluble phenolic oil with 5.85 wt% water soluble constituents.

Table 5.3. Yields of bio-oil stage fractions, noncondensable gases, and char as weight % of biomass feed

red oak pyrolysis products		% yield (wet basis)	moisture, wt %
bio-oil	heavy ends (SF 1 and SF 2)	28.7	3.44
	middle fraction (SF 3 and SF 4)	5.28	13.6
	light ends (SF 5)	28.0	63.0
	total oil	62.0	31.3
non-condensable gas		22.9	0
char		13.2	0
mass balance		98.1	
washed heavy ends	water soluble (sugars from SF 1 and SF 2)	62.7	8.27
	water insoluble (phenolic oil from SF 1 and SF 2)	37.3	19.5
corn stover pyrolysis products		% yield (wet basis)	moisture, wt %
bio-oil	heavy ends (SF 1 and SF 2)	14.9	3.40
	middle fraction (SF 3 and SF 4)	4.87	11.9
	light ends (SF 5)	28.9	74.2
	total bio-oil	48.6	46.2
non-condensable gas		25.4	0
char		20.5	0
mass balance		94.5	
washed heavy ends	water soluble (sugars from SF 1 and SF 2)	39.4	5.38
	water insoluble (phenolic oil from SF 1 and SF 2)	60.6	18.4

The mass yields of the major gas components are given in Table 5.4.

Table 5.4. Yields of major gas components as weight % of biomass feed

feedstock	H_2, wt%	CH_4, wt%	CO, wt%	CO_2, wt%	C_2H_4, wt%	CO_2:CO
red oak	0.027	1.3	9.3	12.3	0.25	1.3
corn stover	0.000	1.1	7.8	15.4	0.18	1.9

5.3.3. ANALYSIS OF PHENOLIC OIL

Table 5.5 provides the analyses of the heavy ends (SF 1 and SF 2) of the bio-oil and the phenolic oil extracted from the heavy ends. The moisture in the heavy-ends SF 1 and SF 2 was very low as produced in the bio-oil recovery system. The washing procedure used to separate the heavy ends into sugars

Table 5.5. Analyses of SF 1 and SF 2 heavy ends and phenolic oils from red oak and corn stover

Analyses	red oak SF 1	red oak SF 2	corn stover SF 1	corn stover SF 2	red oak phenolic oil	corn stover phenolic oil
moisture, wt%	3.37±0.10	3.49±0.35	3.80±0.64	2.53±0.41	17.3±0.62	18.4±0.60
water insolubles, wt%	43.0±2.00	44.4±0.13	55.8±1.07	65.6±0.94	-	-
carbon, wt% db	59.8	61.5	67.1	68.7	65.6	74.4
hydrogen, wt% db	6.26	6.25	6.53	6.64	6.14	6.07
oxygen, wt% db	33.75	31.8	23.3	24.5	28.0	17.4
nitrogen, wt% db	0.117	0.118	1.86	1.35	0.20	NA
Al, ppm db	NA	NA	NA	NA	294	311
Si, ppm db	NA	NA	NA	NA	240	686
K, ppm db	NA	NA	NA	NA	131	359
S, ppm db	NA	NA	NA	NA	47	384
Ca, ppm db	NA	NA	NA	NA	<35	193
Mg, ppm db	NA	NA	NA	NA	<35	133
P, ppm db	NA	NA	NA	NA	<35	94
density, g/mL@40°C	NA	NA	NA	NA	1.20	1.18
viscosity, mm^2/s@40°C	NA	NA	NA	NA	4100	21000
TAN, mg KOH/g	NA	NA	NA	NA	61	NA
filterable Solids, wt%	1.86±0.16	1.65±0.20	5.49±0.07	6.81±0.07	1.37	2.75
acetic, wt% db	0.796±0.026	0.555±0.041	0.763±0.002	0.718±0.002	0.298±0.043	0.409±0.010
formic, wt% db	0.352±0.014	0.255±0.008	0.239±0.003	0.204±0.003	0.198±0.035	0.093±0.002
glycolic, wt% db	0.674±0.068	0.500±0.068	0.697±0.006	0.455±0.003	0.275±0.058	0.202±0.007
propionic, wt% db	0.143±0.005	0.074±0.005	0.131±0.006	-	0.080±0.010	0.095±0.006

and phenolic oil left moisture in the phenolic oil. There was no indication that upgrading of the phenolic oil was adversely affected by this moisture, which phase separated during upgrading. As shown, the water insoluble content was greater for the corn stover SF 1 and SF 2. It is probable that the plugging problems in the reactors, especially for the corn stover oils, was due to the high water insolubles content which likely contained particulate matter. The acid content of the phenolic oils for both red oak and corn stover were very low to start with (≤0.8 wt% db). The water wash removed as much as 56 % of the acid from the water insoluble portion of the heavy ends (SF 1 and SF 2).

The results of GC-MS analysis of the phenolic oils are shown in Table 5.6. The phenolic oil is aptly named as the vast majority of the volatile components are phenolic in nature. For the most part they are syringol (2,6-methoxy phenol) or

Table 5.6. Components in phenolic oils based on GC-MS analysis with relative quantities determined by total ion current

		phenolic oil red oak	phenolic oil corn stover
component	retention time	relative quantity	relative quantity
levoglucosan	19.55-76	5.69	1.44
2,3-dihydrobenzofurans	**16.41-48**	**ND**	**4.17**
ethyl phenol	**15.70**	**ND**	**2.76**
syringol	17.96	5.25	2.21
propenyl syringol	21.51	5.21	1.45
methyl syringol	**19.00**	**3.20**	**0.40**
propenyl guaiacol	19.03	2.88	1.27
unknown	20.22	2.62	0.97
syringol formaldehyde	21.19	2.44	ND
2-propenyl syringol	21.05	2.00	0.40
propenyl syringol	20.57	1.96	0.39
syringol ethanone	21.85	1.45	0.32
guaiacol propenal	21.88	1.31	present
vinyl guaiacol	**17.52**	**1.26**	**2.36**
ethyl guaiacol	17.08	1.10	0.66
methoxy catechol	16.94	1.10	ND
syringol propionaldehyde	23.98	1.08	ND
syringol propenal	23.98	1.08	present
corylone (hydroxymethylcyclopentenone)	13.48	0.78	0.66
propenyl guaiacol	18.57	0.67	ND
guaiacol ethanone	19.47	0.65	ND
hexadecanoic acid	23.22	0.64	present
guaiacol formaldehyde (vanillin)	18.55	0.55	present
catechol	16.30	0.51	present
methyl guaiacol	16.00	0.45	present
guaiacol ethanol (homovanillyl alcohol)	19.17	0.43	ND
hydroxy-propenyl guaiacol	21.29	0.42	ND
guaiacol	14.52	0.42	present
2 and 4 methyl phenol (m,p-cresols)	14.42	0.40	present
hydroxy-propenyl guaiacol	20.34	0.24	ND
methyl syringol bis-dimer	29.08	0.18	present

ND = not detected
bolded components are discussed in the text

guaiacol (2-methoxyphenol) analogs with substituents on the 4 position. There is a significant amount of levoglucosan in both phenolic oils. Comparison of the relative amounts of components shows that most are common in both phenolic oils, at similar concentrations. However, the corn stover phenolic oil

Table 5.7. ^{13}C NMR analysis of bio-oil and phenolic oils

Carbon Type	bio-oil oak	phenolic oil red oak	phenolic oil corn stover
alkyl (0-52 ppm)	11.3%	2.6%	22.4%
carbonyl (192-222 ppm)	5.8%	0.8%	3.7%
carboxyl (170-192 ppm)	6.8%	1.6%	2.6%
ether, alcohols, sugars (53-96 ppm)	25.9%	19.5%	4.3%
phenolic (140-170)	12.8%	22.5%	22.6%
aromatic (96-140 ppm)	37.4%	53.1%	44.4%
ratio aliphatic/aromatic carbon	0.7	0.3	0.4

has a large dihydrobenzofuran fraction, as well as ethyl phenol, which were not found in the red oak phenolic oil. On the other hand, the red oak contained a much larger fraction of methyl syringol while the corn stover had a larger fraction of vinyl guaiacol. It is well known that bio-oil analysis by GC-MS is limited because of the low volatility and thermal instability of much of the product. Because the phenolic oils contain the oligomeric phenols, it was expected to quantify only a fraction of all components. However, this data indicates that the phenolic oils contained volatile monomeric compounds, as well.

The phenolic oil products were also analyzed by ^{13}C Nuclear Magnetic Resonance (NMR) spectrometry. In Table 5.7 the functional groups determined by NMR for an oak fast pyrolysis bio-oil from PNNL can be compared with the red oak phenolic oil and the corn stover phenolic oil. Both phenolic oils contain less non-phenolic type components than the whole bio-oil. The corn stover phenolic oil contains more carbonyl/carboxyl types as well as more carbons, which are not directly bonded with any oxygen. The ratio of aliphatic to aromatic carbons underscores the conclusion that the phenolics are concentrated in the phenolic oil.

5.3.4. HYDROPROCESSING RESULTS

In the first experiment (see Table 5.1) using a single temperature stage with a Pd-Re/C catalyst, the test was short-lived and was terminated after only 6 h due to an increase in pressure drop across the reactor. This effect is typical for unfractionated bio-oil and indicates an excessive amount of catalyst fouling leading to blockage of the reactor flow.[85] In this test the examination of the bed following the test indicated that the blockage may have been due to fine particulate buildup in the fixed catalyst bed rather than fouling by cross linking

85 Elliott, D. C.; Hart, T. R.; Neuenschwander, G. G.; Rotness, L. J.; Zacher, A. H. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. *Environ. Prog. Sust. Energy*, **2009**, *28*(3), (441-449).

reactions of the highly reactive components in the feedstock. Subsequent tests with precious metal catalyst utilized the two-stage hydroprocessing concept, which has been found to alleviate the catalyst fouling difficulty.

Using two sequential beds of different precious metal catalysts at different temperatures, the pressure drop build-up in the reactor was avoided. The first bed was filled with the more active ruthenium metal on carbon extrudate operated at a lower temperature to avoid methane formation (which would be expected at temperatures of 300 °C[86] or above) but still hydrogenate the more active components in the phenolic oil and thereby stabilize the feedstock for higher temperature hydroprocessing. The second bed was filled with a palladium on granular carbon catalyst, which has been found to be useful for bio-oil hydroprocessing.[87] The first test at higher space velocity was ended early when a plug occurred in the feed line, apparently due to particulate in the feedstock being caught in the small diameter (1/8") tubing. The second test at lower space velocity was kept on line for 48 h and terminated as planned when using the mini-hydrotreater with the larger diameter (1/4") feed line.

The hydroprocessing tests showed good results using the two-stage catalytic hydroprocessing strategy. Equal-sized catalyst beds, a Ru/C catalyst bed operated at 140 °C and a Pd/C catalyst bed operated at 370 °C, were used with the entire reactor at 12.5 MPa operating pressure. The hydrogen flow was in great excess, as is typical for hydrotreating.

In the case of the use of a sulfided catalyst the typical catalyst bed fouling seen with fast pyrolysis bio-oil was not found after the test was terminated early, based on pressure drop build-up during the test. Instead, fine particulate was found packed in the catalyst bed at two intervals in the heat-up zone of the bed. Use of the lower space velocity in the second test allowed a longer operating window, even somewhat in excess of the allowance for lower feedstock processing rate, but the bed still became blocked. This result suggests that a filtering preliminary step will be required for processing the phenolic oil. The typical catalyst bed following an experimental run with phenolic oil had evidence of carbonaceous particulate packed "tight" into the catalyst bed, as shown in Figure 5.5. The balance of the catalyst beds were free flowing and easily removed from the reactor tube for analysis.

86 Elliott, D. C.; Hart, T. R. Catalytic hydroprocessing of chemical models for bio-oil. *Energy Fuels*, **2009**, *23*, (631-637).

87 Elliott, D. C.; Hart, T. R.; Hu, J.; Neuenschwander, G. G. Palladium Catalyzed Hydrogenation of Bio-Oils and Organic Compounds. U.S. Patent #7,425,657, issued September 16, 2008.

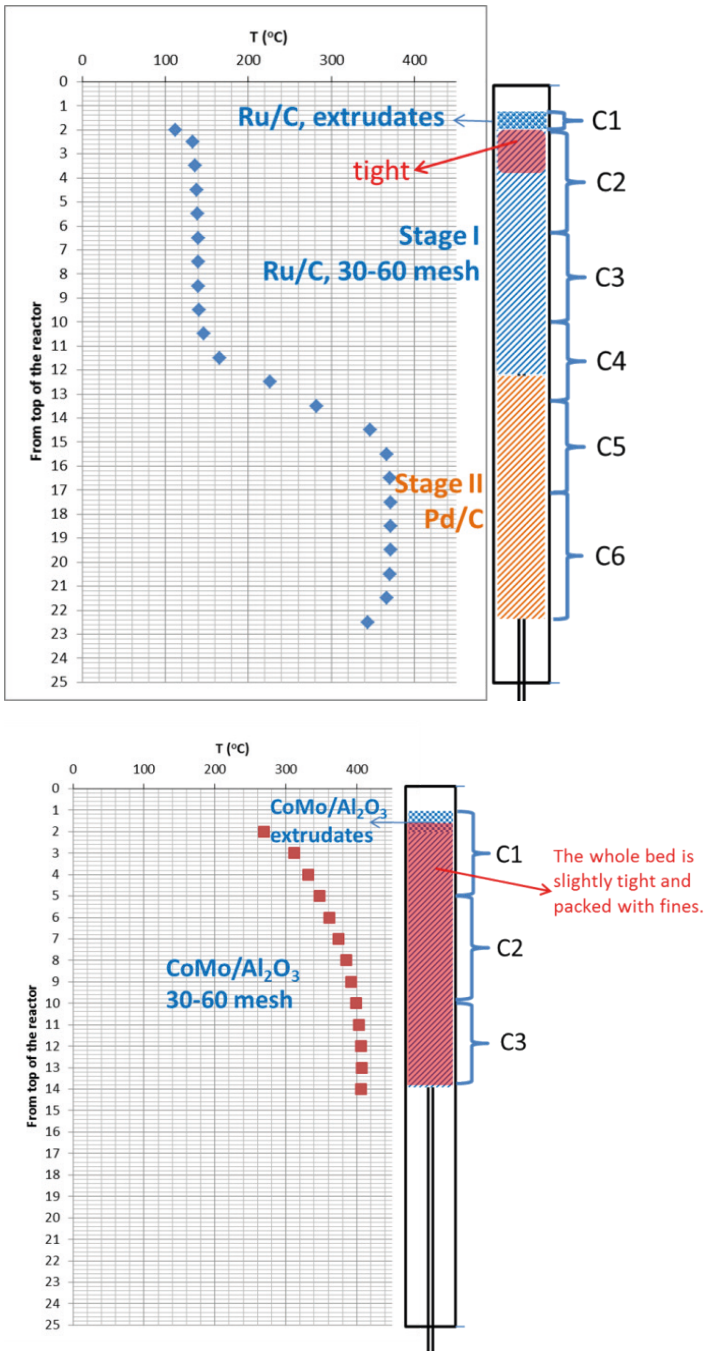


Figure 5.5. Schematic of the catalyst beds after use with red oak phenolic oil

Table 5.8. Results from hydroprocessing red oak phenolic oil with Ru-Pd catalysts

TOS	mass yield, oil product	carbon yield, oil product	oil product density	gas yield	produced water yield	H_2 consumed	mass balance	carbon balance
	g dry/g dry feed	g C/g C in feed	g/ml	g per g dry feed	g per g dry feed	g H_2/g dry feed	%	%
12-18 h[a]	0.585	0.719	0.87	0.074	0.164	0.042	86.9	80.5
24-30 h[b]	0.599	0.748	0.85	0.104	0.217	0.037	94.6	84.8
36-42 h[b]	0.657	0.812	0.88	0.083	0.189	0.039	95.2	90.4

[a] high LHSV 0.2 in each bed (0.1 total)
[b] low LHSV 0.1 in each bed (0.05 total)

Table 5.9. Results from hydroprocessing red oak phenolic oil with CoMoS catalyst

TOS	mass yield, oil product	carbon yield, oil product	oil product density	gas yield	produced water yield	H_2 consumed	mass balance	carbon balance
	g dry/g dry feed	g C/g C in feed	g/ml	g per g dry feed	g per g dry feed	g H_2/g dry feed	%	%
4-5h[a]	0.617	0.805	0.835	0.099	0.247	0.046	93.7	90.1
12-18h[b]	0.614	0.792	0.835	0.113	0.307	0.074	96.8	92.1

[a] high LHSV 0.5
[b] low LHSV 0.2
For comparative data for whole bio-oil from pine see reference #75.

Mass balances for red oak runs ranged from 87 to 97 % for the steady-state windows calculated, with carbon balances somewhat lower, ranging from 80 to 92 %. Since the liquid and gaseous products were all measured, the carbon loss can be attributed to experimental error and to deposits on the catalyst particles. The process results for hydrotreating with the two catalyst schemes are shown in Tables 5.8 and 5.9. The hydrogen consumption values are in the range expected for bio-oil hydrotreating. The somewhat higher numbers for the CoMoS test can be explained by the higher temperature operation resulting in better deoxygenation, density reduction and gas formation.

The products from the red oak phenolic oil tests are shown in Table 5.10. These catalytic hydroprocessing experiments resulted in mostly deoxygenated products but required long processing residence times resulting in low processing space velocities. The precious metal catalysts, which were operated at lower space velocity but also lower temperature, resulted in more saturated product oil (higher hydrogen to carbon ratio), but the sulfided CoMo catalyst

Table 5.10. Hydrotreater feed/product analyses for red oak phenolic oil tests (dry basis)

	C (wt%)	H (wt%)	O (wt%)	H/C	N (wt%)	S (wt%)	moisture (wt%)	density g/ml @40°C
Feedstock	71.03	6.42	22.36	1.08	0.17	0.02	14.50	1.18
Products								
Pd/Re 2-4 h	83.57	12.60	1.70	1.79	<0.05	<0.005	0.20	0.819
Pd/Re 4-6 h	83.10	11.75	3.05	1.68	<0.05	<0.005	0.20	0.878
Ru/Pd hi LHSV 12-18 h	81.12	12.11	5.11	1.77	<0.05	<0.005	0.22	0.870
Ru/Pd lo LHSV 24-30 h	82.09	12.40	3.43	1.80	<0.05	<0.005	0.08	0.846
Ru/Pd lo LHSV 36-42 h	81.38	11.73	4.84	1.71	0.045	0.013	0.23	0.880
CoMoS hi LHSV 4-5 h	79.86	10.78	0.40	1.60	<0.05	<0.005	0.20	0.835
CoMoS lo LHSV 6-12 h	79.01	12.55	1.90	1.89	<0.05	<0.02	<0.01	0.792
CoMoS lo LHSV 12-18 h	82.26	12.00	1.85	1.73	<0.05	<0.02	<0.01	0.835

was more effective in hydrodeoxygenation. The low overall recovery of elements, (C+H+O)<100, in the high LHSV test with the CoMoS catalyst along with the significant amount of dissolved water in the product, suggests that the oxygen content was actually higher than reported by the analysis. Hydrotreating of the nitrogen content was also effective, being reduced below the level of detection. The sulfur level is quite low in the phenolic oil, but its removal to below the level of detection was also determined.

The yield of hydrocarbon liquids, when normalized for the deficient carbon balance, ranges from 0.88 and 0.90 g C/g C in feed. These numbers are higher than reported for hydrotreating of whole red oak bio-oil, wherein the results are around 0.82, although the catalyst bed composition was not perfectly comparable.[83]

^{13}C NMR analysis of the products also shows dramatic changes in carbon types (Table 5.11). There are very few oxygenates left. The Ru/Pd two-stage catalyst bed was most active for saturating the hydrocarbon products. The shift in the entries in the two last columns shows the catalyst deactivation as the test progressed, wherein the deoxygenation and saturation were less prevalent.

Two of the hydrotreated products from red oak phenolic oil (CoMo 12-18 h and Ru-Pd 24-30 h) were also analyzed by gas chromatography simulated distillation (SimDist ASTM D2887). This method is standardized for analysis of diesel fuels, so its application to these products, which are more comparable to sweet crude, shows the important difference in the low temperature

Table 5.11. ^{13}C NMR analysis of hydrotreated red oak phenolic oil

carbon type	PdRe	Ru/Pd high	Ru/Pd low	Ru/Pd low	CoMoS high
alkyl (0-52 ppm)	80.4%	88.5%	89.9%	88.4%	68.0%
carbonyl (192-222 ppm)	0.3%	0.6%	0%	0.8%	0%
carboxyl (170-192 ppm)	0%	1.2%	0.5%	0.9%	0.4%
ether, alcohols, sugars (53-96 ppm)	1.4%	1.3%	1.2%	0.3%	0%
phenolic (140-170)	2.6%	1.0%	1.1%	2.6%	3.4%
aromatic (96-140 ppm)	15.3%	7.5%	7.3%	7.0%	28.1%
ratio aliphatic/aromatic carbon	4.5	10.4	10.7	9.2	2.2

distillate range. As shown in Figure 5.6, there was a significant portion of the hydrotreated products that falls in the gasoline range. There was a small tail in each product that fell into the distillation range of heavy oil, but not much more than was found in the diesel standard fuel.

A hydrotreating test was also completed with the corn stover phenolic oil using the non-sulfided catalysts. Initial tests with the corn stover phenolic oil all ended after only a short period of time on stream without useful results because of plugging in the feed line by particulate. A successful process test using the 2-stage catalyst bed (Ru/C @ 140 °C and Pd/C @ 370 °C, all at 12 MPa) could only be completed after filtering the phenolic oil. The filtration could only be accomplished with dilution of the phenolic oil with 10 wt% isopropanol. When the diluted and filtered phenolic oil was used as the feedstock, the test was operated for 48 h and was terminated as planned, similar to the red oak phenolic oil test. The used catalyst bed exhibiting no pressure drop build-up is shown schematically in Figure 5.7. The entire test was operated at the low liquid hourly space velocity of 0.1 L/L/h in the isothermal portion of each catalyst bed.

The results for the corn stover phenolic oil hydrotreating test are given in Table 5.12 and the feed and product analyses are shown in Table 5.13. The yield of hydrocarbon liquids, when normalized for the deficient carbon balance, are 0.790 and 0.821 g C/g C in feed, for the two cases given. These numbers are higher than reported for hydrotreating of whole bio-oil produced from a similar herbaceous feedstock, switchgrass, wherein the results are around 0.75.[83]

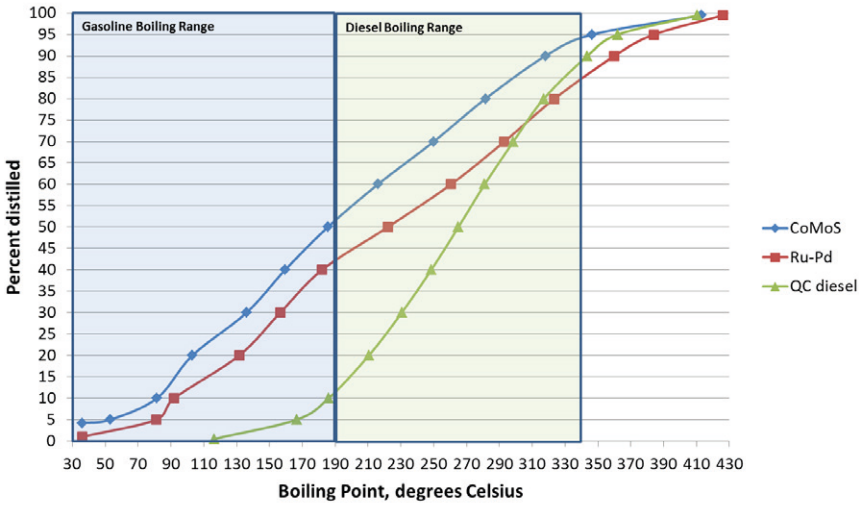


Figure 5.6. SimDist of hydrotreated red oak phenolic oil from low LHSV tests

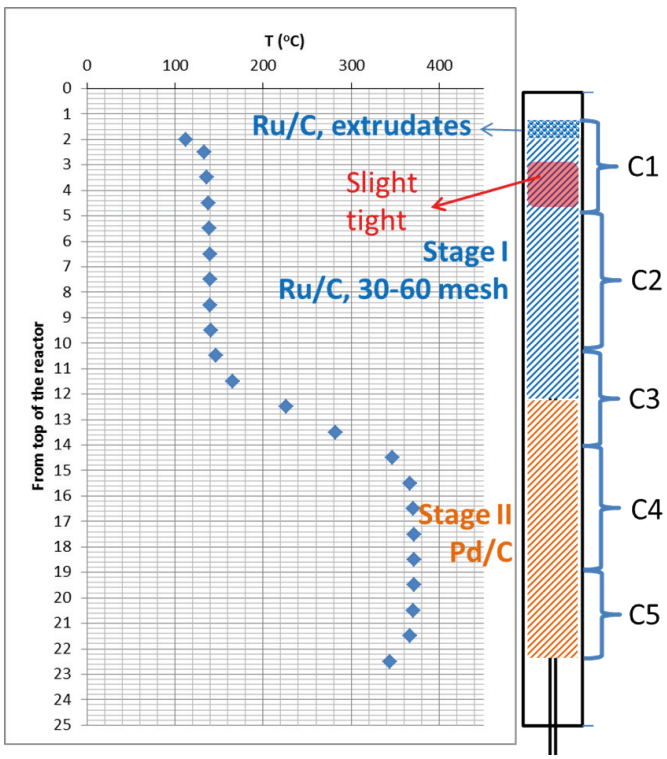


Figure 5.7. Schematic of the catalyst beds after use with corn stover phenolic oil

Table 5.12. Results from hydroprocessing corn stover phenolic oil

TOS and duration	mass yield, oil product	carbon yield, oil product	oil product density	gas yield	produced water yield	H_2 consumed	mass balance	carbon balance
	g dry/g dry feed	g C/g C in feed	g/ml	g per g dry feed	g per g dry feed	g H_2/g dry feed	%	%
24-30h	0.533	0.632	0.825	0.128	0.221	0.045	91.8	80.0
36-42h	0.580	0.679	0.857	0.111	0.215	0.040	94.6	82.7

Table 5.13. Hydrotreater feed/product analyses for corn stover phenolic oil test

	C (wt%)	H (wt%)	O (wt%)	H/C	N (wt%)	S (wt%)	moisture (wt%)	density g/ml @40°C
diluted phenolic oil, as fed	70.91	7.44	20.59	1.17	1.66	0.04	10.97	1.15
24-30 h product	84.07	13.89	1.98	1.96	0.07	<0.04	0.00	0.825
36-42 h product	83.03	13.07	3.38	1.87	0.53	<0.04	0.38	0.857

5.4. DISCUSSION

The red oak phenolic oil performed well for up to 48 h when using certain catalyst configurations but was still susceptible to catalyst bed fouling and plugging in other cases. The phenolic oil, like phase-separated "pyrolytic lignin," has some advantages for upgrading compared to whole bio-oil, including higher yields of gasoline and diesel range molecules and less tendency to coke.[88] Use of the mini-hydrotreater with the larger diameter feed line (1/4" versus 1/8") facilitated operation by avoiding feed line blockage by particulate. However, the unfiltered corn stover phenolic oil had sufficient filterable solids, which resulted in catalyst bed blockage in any case. Filtering of the solids from the corn stover phenolic oil after dilution of 10 wt% isopropanol resulted in a smooth operation, similar to that of the red oak phenolic oil.

The products from the tests with different catalysts and phenolic oil feedstock were all similar. The light oil phase product was sufficiently hydrotreated so that nitrogen and sulfur were at or below the level of detection, while the residual oxygen content was low, less than 5 %. The density of the products varied from 0.79 g/mL up to 0.88 g/mL over the period of the longer tests,

88 Elliott, D. C.; Neuenschwander, G. G.; Hart, T. R. Hydroprocessing bio-oil and products separation for coke production. *ACS Sust. Chem. Eng.*, **2013**, *1*, (389-392).

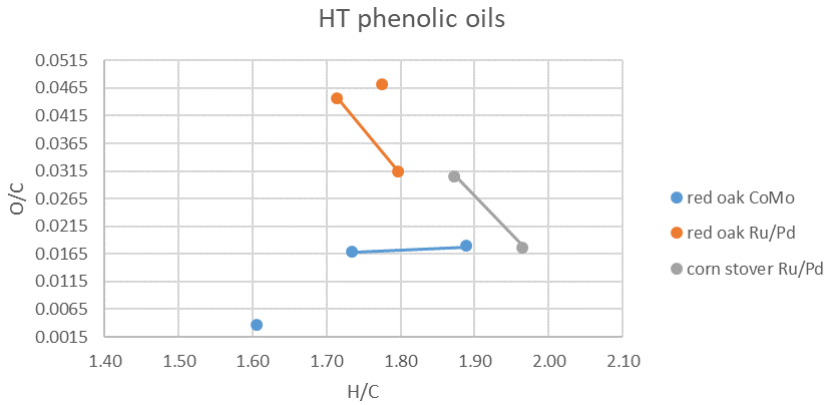


Figure 5.8. van Krevelen plot of hydrotreated products from phenolic oil products

which correlated with a change of the hydrogen to carbon atomic ratio from 1.9 down to 1.7, suggesting some loss of catalyst activity through the test.

For the purposes of this thesis, a van Krevelen analysis has been applied to the hydrotreating products. As seen in Figure 5.8, the change in product compositions over the time of the experiment (42 h) for the Ru/Pd catalyst tests at low LHSV (0.1) suggests a trend (but only two data points) to lower quality products, i.e. loss of catalyst activity. The test with the red oak phenolic oil using a CoMo catalyst (at higher LHSV) suggests a mixed effect over time on stream resulting in a hydrotreated product with a lower O content but with less hydrogenation of the components. The two single data points for higher LHSV do not seem to correlate with the others.

The product gas composition showed some interesting variations with catalyst, feedstock, and space velocity, as shown in Table 5.14. The composition is presented on a hydrogen-free basis and shows only the product gases. For these tests there was a large excess of hydrogen, as is typical for hydrotreating, amounting to about 95 vol % of the process off-gas. There are significant differences between the two phenolic oil types in that hydrotreatment of red oak phenolic oil produced much less propane and more methane. The propane is most likely a result of the isopropanol solvent present in the test. The Re-promoted Pd catalyst resulted in a much higher methane product than the Pd alone (the Ru was operated at low temperature to minimize its well-known methanation activity) while the CoMoS catalyst also produced more methane, as well as the other hydrocarbons, probably due to its higher temperature operation. CO production is associated with the use of the Ru-Pd catalyst system

Table 5.14. Product gas composition from hydroprocessing phenolic oil, volume percent (H_2-free basis)

TOS	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO	CO_2
red oak PdRe							
4-6 h[a]	71.3	5.5	5.6	0.7	0	0	16.9
red oak Ru-Pd							
12-18 h[c]	23.0	4.4	5.4	0	0	19.7	47.6
24-30 h[d]	17.9	3.4	5.0	2.4	1.0	11.8	58.6
red oak CoMoS							
4-6 h[a]	52.0	8.0	11.0	2.8	0.4	0	25.9
12-18 h[b]	53.6	12.6	23.4	3.8	2.2	0	4.4
corn stover Ru-Pd							
24-30 h[d]	11.9	6.3	55.2	2.2	0	9.8	14.6

a high LHSV 0.5
b low LHSV 0.2
c high LHSV 0.2/0.2
d low LHSV 0.1/0.1

with either phenolic oil because of the lesser methanation activity of Pd. The product gas would likely be recycled through a membrane recovery system for hydrogen, followed by processing through a steam reformer to produce more hydrogen.

The variation in the mineral content in the phenolic oils and the fate of the minerals in the hydroprocessing tests were determined. In the case of the red oak phenolic oil, the mineral content is primarily Al and Si with lesser amount K and S (see Table 5.5). Analysis of the catalyst bed fractions after the tests (see Table 5.15) shows that mineral deposition is noticeable for both catalyst systems. In the test with Ru-Pd two-stage bed, the amount of K, as well as Ca, Fe, and Na, was actually lower in the front-end catalyst bed of Ru/C after use, suggesting that those elements are transported from the bed. In the second bed composed of the Pd/C catalyst, those four elements are also reduced from starting catalyst levels, suggesting that they were flushed from the second bed as well. Significant deposits of Si and Al from the phenolic oil are found in the second portion of the Ru/C catalyst bed, which correlates with the portion of "slightly tight" catalyst ("slightly tight" in this instance means that the catalyst particles adhered to each other, apparently due to a light deposit, and did not flow freely from the reactor tube without prodding). Further in the reactor, they are reduced in the Pd/C catalyst bed from the levels measured in the fresh Pd/C, perhaps suggesting their higher solubility at higher

Table 5.15. Catalyst analyses before and after hydroprocessing red oak phenolic oil (ppm, dry basis)

	Ru/C	used Ru/C		used Pd/C		Pd/C	$CoMo/Al_2O_3$	used $CoMo/Al_2O_3$		
	fresh	C2*	C3*	C5*	C6*	fresh	fresh	C1*	C2*	C3*
Al	695	1145	786	630	522	1040	386000	283900	314100	331450
Ca	417	262	157	192	367	484	987	740	842	931
Co	NA	NA	NA	NA	NA	NA	33430	26560	28940	30400
Fe	199	110	172	368	352	659	75	853	270	202
K	443	238	190	210	708	1197	73	592	96	88
Mg	281	150	149	187	355	463	588	438	470	500
Na	74	<35	<35	<35	727	1363	254	332	238	236
Ni	<35	<35	<35	<35	<35	<35	495	405	424	499
P	<35	<35	<35	45	39	82	11940	7728	8276	8764
Mo	<35	<35	<35	<35	<35	<35	68465	55030	60445	63065
Si	1026	2408	1070	1124	764	1361	1504	2179	2238	1764
S	3145	3060	2054	247	94	76	1036	34585	46470	47910
Ru	51970	40715	45560	83	<35	<40	<45	<45	<45	<45
Pd	<40	<35	<35	3380	3936	5100	<45	<45	<45	<45

NA = not analyzed
* numbering indicates different positions in catalyst bed as shown in Figure 5.5

temperature. There are no signs of the other metals from the reactor walls (Ni, Cr, Mo), apparently suggesting that corrosion of the reactor walls is not significant. The ruthenium analysis reports a lower level in the used catalysts. Carbon deposition in the pores of the catalyst has been determined to be the agent diluting the ruthenium concentration rather than actual leaching of the metal from the support.

This effect was confirmed previously with the CoMo catalyst wherein the carbon deposition was quantified by direct elemental analysis.[83] In the catalyst bed of sulfided CoMo on Al_2O_3, the Ca is only reduced (at levels similar to Co, Mo, Al) by the dilution of the catalyst with carbon particulate, while the K, Fe, and Na are actually deposited onto the catalyst in the front end of the bed. Similar deposition of Si is also evident. The other catalyst components Al, P, and W show evidence of leaching from the catalyst as their relative amounts are less than the diluted Co and Mo major catalyst components.

Sulfur analysis of samples of the catalyst gave conflicting results relative to the sulfidation of the precious metal catalysts. In the red oak phenolic oil case, the highest sulfur loading of the Ru catalyst is consistent with a 12 % sulfidation as RuS_2 but it is lower than the fresh catalyst analysis. A typical level, based on

Table 5.16. Catalyst analyses before and after hydroprocessing corn stover phenolic oil (ppm, dry basis)

	Ru/C	used Ru/C			used Pd/C		Pd/C
	fresh	C1*	C2*	C3*	C4*	C5*	fresh
Al	635	417	404	487	986	504	861
Ca	252	542	177	188	241	462	586
Fe	143	67	92	175	464	271	190
K	318	211	203	228	476	248	292
Mg	243	148	137	194	349	284	380
Na	63	<40	<40	<40	93	127	162
Si	753	724	492	481	648	820	1111
S	1986	3974	2634	1964	522	703	1824
Ru	60230	44535	43210	44310	169	<40	<40
Pd	<40	<40	<40	673	11995	11405	21065

* numbering indicates different positions in catalyst bed as shown in Figure 5.7

literature reports is 40 % Ru sulfidation in a hydrothermal environment.[89] The sulfur loading of the Pd catalyst relative to the fresh catalyst is evident but is much less than on the Ru catalyst by an order of magnitude. Also, sulfidation of the CoMo catalyst was verified wherein the sulfur content was equivalent to molar ratio equivalent to the CoMo loading ranged from 1.1 to 1.3 over the catalyst bed. The ratio of S to metals in the CoMo catalyst suggested that the metals were 70 to 83 % of fully sulfided.

In the case of the corn stover phenolic oil, trace mineral content was more significant, about three times the Al and K, with eight times as much S and significant amounts of Ca, Mg and P, which were not measureable in the red oak phenolic oil (see Table 5.5). However, it is likely that most of this mineral matter was removed during the solvent dilution and filtration prior to hydrotreating. Analysis of the catalyst bed fractions after the tests (see Table 5.16) showed that mineral deposition was not significant when processing the corn stover phenolic oil. The amount of Ca was higher at the front of the first catalyst (Ru/C) bed, and K was higher at the front of the second catalyst (Pd/C) bed, but in the balance of the beds they were actually lower than in the fresh catalysts. Si was actually lower in the catalyst beds after use. The amount of sulfur was

89 Dreher, M.; Johnson, B.; Peterson, A. A.; et al. Catalysis in supercritical water: Pathway of the methanation reaction and sulfur poisoning over a Ru/C catalyst during the reforming of biomolecules. *J. Catal.* **2013**, *301*, (38-45)

elevated in the front of the Ru bed, but was actually lower in the used Pd bed, compared to the fresh Pd catalyst. These results suggest that sulfidation of the Ru catalyst may be a significant long-term operational problem, while Pd may be more resistant in this operating environment. The analyses seem to show that the K, Al, and Fe all migrated from the Ru bed to the Pd bed.

6

Hydrotreating of the Product Liquids from the bioCRACK Pyrolysis Process

Schwaiger, N.; Siebenhofer, M.; Elliott, D.C.; Wang, H.; Ritzberger, J.; Pucher, P. 2015. "Hydrocarbon Liquid Production via the bioCRACK Process and Catalytic Hydroprocessing of the Product Oil." **Green Chem.** *17*, 2487-2494, web published February 13, 2015, DOI: 10.1039/c4gc02344g.

6.1. INTRODUCTION

Fast pyrolysis of biomass is a viable technology for the direct production of liquid fuels.[90] Liquid phase pyrolysis of biomass is an alternative technology to fast pyrolysis. Although product classes, such as liquid phase bio-oil and biochar, are similar, the differences in operation and product composition are significant. Liquid phase pyrolysis is usually powered with liquid heat carrier.[91] This heat carrier limits the operation temperature to less than 400 °C according to the boiling point and thermal stability. This temperature limit leads to a higher amount of biochar and less liquid phase bio-oil production with higher water content and acid number. A major advantage of liquid phase pyrolysis over fast pyrolysis in fluidized bed operation is elevated heat transfer in the liquid heat carrier phase. Also, biochar and inorganics are retained in the liquid heat carrier. Liquid phase bio-oil is not contaminated with solids. Thus, hot vapor filtration[92] for dust removal from the vapor phase is not needed.[93] However, depending on the heat carrier biomass is partially dissolved in it.

The Bio-oil product from fast pyrolysis and liquid phase pyrolysis, however, is not of sufficient quality for direct use as petroleum refinery feedstock. Catalytic hydroprocessing has been developed to convert the highly oxygenated bio-oil components into hydrocarbons.[94] Conventional hydrotreating processes cannot be directly applied for upgrading of fast pyrolysis bio-oil. Specifically, the necessity of a two-temperature strategy was identified.[95]

The objective of this research project was to develop a catalytic hydrotreating process for the production of crude petroleum refinery feedstock from biomass, specifically from condensate of the bioCRACK process. From bioCRACK pyrolysis two different fractions of condensate, high aqueous bio-oil and dehydrated bio-oil, are collected. These feedstocks need hydroprocessing to produce a refinery compatible hydrocarbon-like feedstock. Previous hydrodeoxygenation studies have been performed in a batch reactor with the bioCRACK bio-oil and dehydrated bio-oil using precious and base metal

90 A.V. Bridgwater, *Biomass and Bioenergy*, 2012, **38**, 68–94.

91 N. Schwaiger, R. Feiner, K. Zahel, A. Pieber, V. Witek, P. Pucher, E. Ahn, P. Wilhelm, B. Chernev, H. Schröttner, and M. Siebenhofer, *BioEnergy Res.*, 2011, **4**, 294–302.

92 D. Mohan, C. U. Pittman, and P. H. Steele, *Energy & Fuels*, 2006, **20**, 848–889.

93 N. Schwaiger, V. Witek, R. Feiner, H. Pucher, K. Zahel, a Pieber, P. Pucher, E. Ahn, B. Chernev, H. Schroettner, P. Wilhelm, and M. Siebenhofer, *Bioresour. Technol.*, 2012, **124**, 90–4.

94 D. C. Elliott, *Energy & Fuels*, 2007, **21**, 1792–1815.

95 E. Baker and D. Elliott, *US Pat. 4,795,841*, 1989.

Figure 6.1. bioCRACK pilot plant at OMV refinery Vienna/Schwechat

catalysts at lower temperature. The process resulted in a partially deoxygenated bio-oil with some improvements in reduced heavy product compared to conventional fast pyrolysis bio-oil hydroprocessing.[96]

Investigations focused on hydrotreating of condensate from liquid phase pyrolysis of spruce wood pellets. The bio-oils were produced in a bioCRACK reactor located at the OMV refinery complex in Schwechat, Austria. The bio-oil products were hydrotreated in a bench-scale, continuous-flow, packed-bed catalytic reactor at Pacific Northwest National Laboratory (PNNL).

6.2. EXPERIMENTAL

The pyrolysis experiments were performed in the BDI-BioEnergy International AG bioCRACK pilot plant facility at OMV refinery Vienna/Schwechat. Figure 6.1 shows an image of the pilot plant facility. Spruce pellets were the feedstock for liquid phase pyrolysis. VGO (vacuum gas oil) was the liquid heat carrier. The biomass feed rate was between 60-100 kg/h. The ratio of biomass and VGO varied between 1:3 and 1:6. Pyrolysis temperature was between 350-400 °C.

96 H. Pucher, N. Schwaiger, R. Feiner, P. Pucher, L. Ellmaier, and M. Siebenhofer, *Int. J. Energy Res.*, 2014, **38**, 1964–1974.

The flow sheet of the bioCRACK pilot plant is shown in Figure 6.2. Biomass and liquid heat carrier oil are fed simultaneously into the impregnator. From there a biomass heat carrier slurry is transferred into the reactor 1 and 2 were the biomass is immediately heated to 375 °C. The biogenic and the fossil vapors are cooled in the condenser. The settling vessel separates the condensed vapors into an aqueous bio-oil fraction and the non-polar bioCRACK oil fraction. In the following distillation step high boiling heat carrier residues are separated from the nonpolar bioCRACK oil fraction. After pyrolysis the heat carrier is separated from biochar.

For further lab scale processing the residual heat carrier is separated from biochar by solid liquid extraction. Biochar can then undergo liquefaction.[97,98,99]

6.2.1. BIOCRACK BIO-OIL DEHYDRATION

Due to the high water content of aqueous bio-oil, dehydration was tested to raise the energy content and to lower transport volume. Dehydration of flash pyrolysis bio-oil was already tested,[100,101] but there is no data available for liquid phase pyrolysis bio-oil.

Dehydration was performed by short path distillation. The apparatus had a heat exchanger surface of 0.1 m². The heat carrier operating temperature was 130 °C and operating pressure was 130 mbar. It has been reported,[102] that upgrade of bio-oil distillate with ethanol may increase economic revenue.

6.2.2. HYDROPROCESSING

bioCRACK bio-oil samples of dehydrated bio-oil and a native bio-oil were shipped to PNNL. The bio-oils were hydroprocessed in a mini-hydrotreater (see Figure 6.3). The hydrotreater is a single pass, co-current, continuous, down-flow reactor. The system can operate up to 12.4 MPa (1800 psig) with a maximum catalyst temperature of 400 °C. The setup consists of a gas feed and liquid feed system, the reactor and a gas-liquid separation system. The gas feed system consists of a manifold for feeding hydrogen through one mass flow controller and helium through a second mass flow controller. The liquid

97 R. Feiner, N. Schwaiger, and H. Pucher, *RSC Adv.*, 2014, **4**, 34955.

98 R. Feiner, N. Schwaiger, H. Pucher, L. Ellmaier, P. Pucher, and M. Siebenhofer, *RSC Adv.*, 2013, **43**, 1–6.

99 R. Feiner, N. Schwaiger, H. Pucher, L. Ellmaier, A. Reiter, M. Derntl, T. Glatz, P. Pucher, and M. Siebenhofer, *BioEnergy Res.*, 2014, **7**, 1343–1350.

100 S. Wang, Y. Gu, Q. Liu, Y. Yao, Z. Guo, Z. Luo, and K. Cen, *Fuel Process. Technol.*, 2009, **90**, 738–745.

101 Z. Guo, S. Wang, Y. Gu, G. Xu, X. Li, and Z. Luo, *Sep. Purif. Technol.*, 2010, **76**, 52–57.

102 S. Wang, Q. Cai, X. Wang, and L. Zhang, *Energy & Fuels*, 2013.

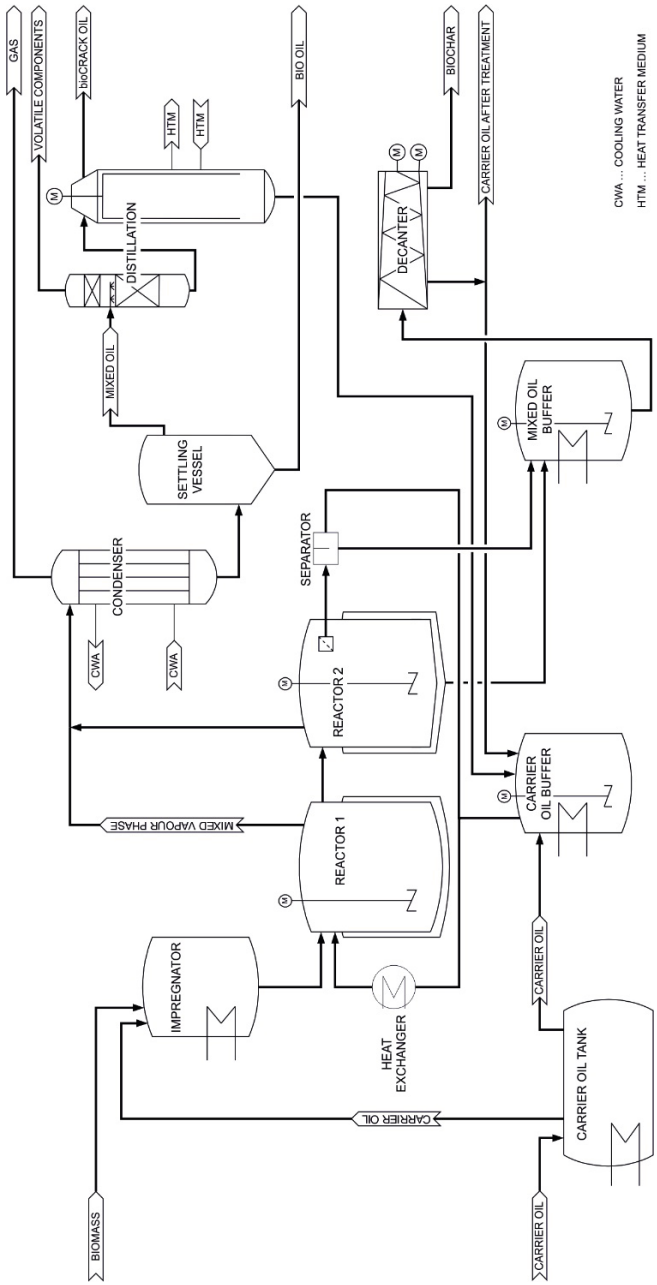


Figure 6.2. Process scheme of the bioCRACK pilot plant Vienna/Schwechat

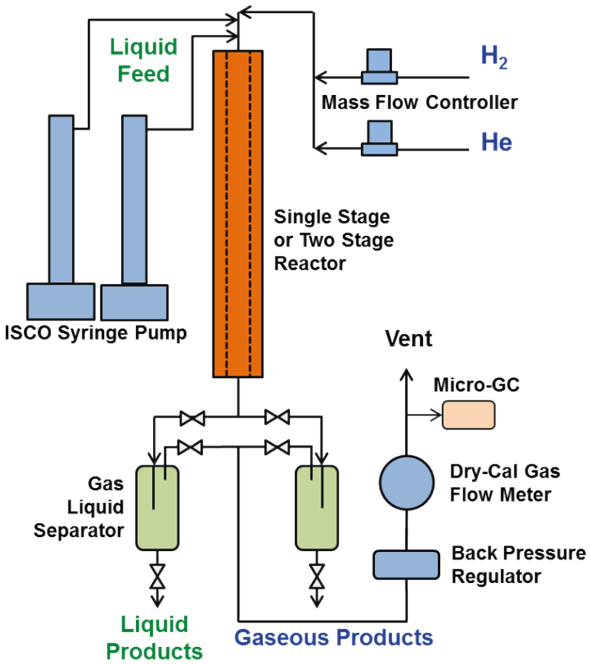


Figure 6.3. Schematic of the mini-reactor hydrotreater system

bio-oil feedstock is delivered to the pressurized reactor system by two high pressure ISCO syringe pumps. The tubular fixed-bed catalytic hydrotreater is made of 316 stainless steel, 13 mm (1/2") internal diameter by 64 cm long with 40 ml capacity for single stage heater or 24 + 24 ml capacity for two-stage hydrotreating. The reactor is heated by a single heating zone. The liquid feedstock and hydrogen gas entered the top of the catalyst bed and passed downward through the bed in a trickle flow. The temperature of the catalyst bed was monitored by thermocouples in a thermocouple well (5 mm (3/16") tubing). After exiting the catalytic reactor, the liquid products were separated from the gaseous products in one of two pressurized and cooled traps placed in parallel flow downstream of the reactor system. Periodically liquid samples were collected when switching collection vessels and venting/draining the trap. The recovered liquid products were phase-separated, weighed, and sampled for further analysis. The off-gas passed a back-pressure regulator and was then directed through a DryCal gas meter to monitor the gas flowrate. Periodically gas samples were analyzed by an online Inficon Micro-GC 3000 4-Channels micro gas chromatograph with molecular sieve, Plot U, Alumina, and Stabilwax

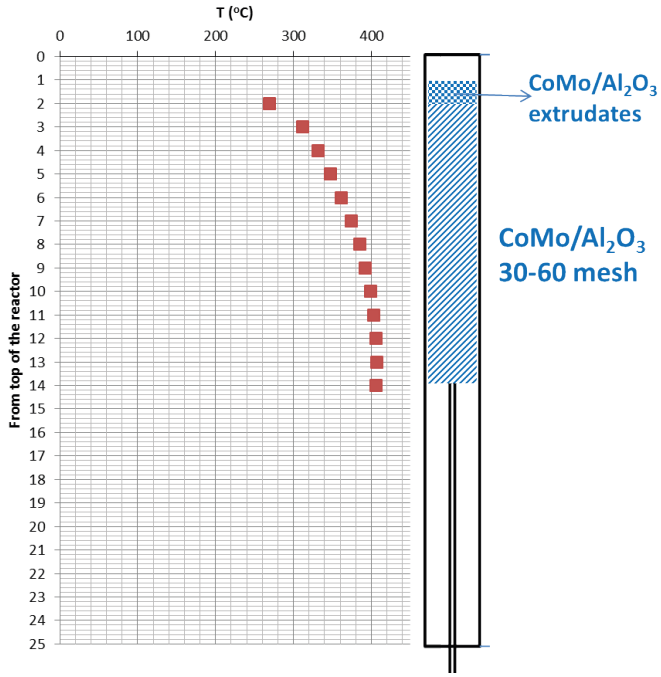


Figure 6.4. Schematic of the catalyst bed in the mini-hydrotreater reactor

columns. Prior to each hydrotreating test, the micro GC was calibrated using a calibration gas standard.

Campaigns were performed for each feed over the course of a five-day test, and the products and feed were collected to assess performance for each bio-oil for comparison with the results obtained from processing of fast pyrolysis bio-oil.

The hydroprocessing tests performed well with CoMo catalyst, sulfided *in situ*. The reactor tube containing the catalyst was heated to 150 °C in H_2 flow, followed by a temperature ramp from 150 °C to 350 °C over 3 h and H_2 flow and sulfiding agent (35 % di-tertiarybutyl-disulfide (DTBDS) in decane). Then temperature was raised to 400 °C and held constant for 5 h with H_2 and sulfiding agent flow.

For the hydroprocessing tests the flow ratio of H_2/liquid was 2508 L H_2 (L bio-oil)$^{-1}$. The operating pressure was 12.1 MPa (1750 psi). The bio-oil feedstock was spiked with DTBDS equaling 150 ppm of sulfur. Figure 6.4 shows a schematic of the catalyst bed with a super-imposed temperature profile for the single stage testing mode. The temperatures were monitored at the center

line of the catalyst bed by a thermocouple which was adjustable within a full length thermowell. The isothermal part of the catalyst bed is clearly shown and the length of the isothermal part of the catalyst was used to calculate the space velocity.

6.2.3. ANALYTICAL METHODS

The feedstock and bio-oil products, as produced, were analyzed at BDI-BioEnergy International AG. All liquid and solid products and the feed were characterized by elemental analysis in CHN mode with a Vario macro CHNO-analyzer, from Elementar Analysensysteme. The heat carrier and entrained heat carrier composition and boiling characteristics were determined with a GC-SimDis MXT 2887, 10m column from Restek and Agilent 7890A GC. Water was measured with GC-TCD. Determination of biomass volatiles was done according to Standard EN 15148. ^{14}C analytics was done by Beta Analytic Limited. For CO and CO_2 detection an ABB gas analyser with an uras 26 infrared photometer was used and Oxygen was measured with a Magnos 206 detector.

The bio-oils and hydrotreated products were characterized at PNNL for elemental analysis, including C, H, N, O, & S, Total Acid Number (TAN), water content, metals content, and by GC-MS. Using a DB-5 column over a temperature program, separation of the bio-oils was performed and mass spectrometric analysis undertaken with a Mass Selective Detector.

6.3. RESULTS

6.3.1. FEEDSTOCK

Results from the feedstock analyses are shown in Table 6.1.

6.3.2. RESULTS OF LIQUID PHASE PYROLYSIS ACCORDING TO THE BIOCRACK PROCESS

The yield of the major products (oil, char, and gas) of the bioCRACK process is shown in Figure 6.5. The figure shows the mass balance based on ^{14}C analysis of an experiment at 375 °C with a biomass feed of 65 kg/h. The amount of biomass fed, bio-oil fractions, and char were determined gravimetrically.

During liquid phase pyrolysis in the bioCRACK process biochar (BCH) and gas/vapor is formed from biomass constituents. Table 6.2 shows the elemental composition of the product streams. Differently to flash pyrolysis three liquid

Table 6.1. Composition of feedstock

	proximate analysis (wt%)			ultimate analysis (wt%)			
	volatiles	fixed Carbon	ash	C	H	N	O by diff.
spruce pellets	84.94	14.68	0.38	50.67	6.30	0.04	42.99

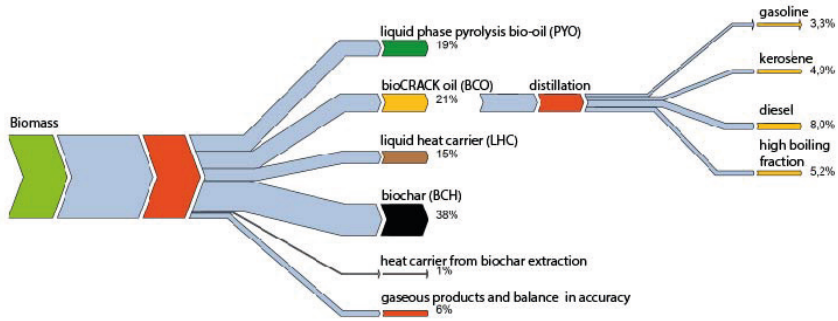


Figure 6.5. Biogenous carbon mass balance of liquid phase pyrolysis as performed in the bioCRACK pilot plant at OMV Refinery Vienna[103]

product streams are formed in the bioCRACK process. The first fraction is a high boiling fraction of decomposed biomass, which is dissolved during liquefaction into the heat carrier. 15 (wt%) of the biogenous carbon feed is solved into this fraction and the concentration of biogenous carbon in this fraction is 2.0 (wt%). The second liquid fraction is the so-called bioCRACK oil (BCO). This is a non-polar phase of biomass decomposition products and the degraded heat carrier. During pyrolysis 21 % of the biogenic carbon from biomass is directly dissolved into this hydrocarbon fraction and the concentration of biogenous carbon is 6.7 (wt%). The bioCRACK oil can be fractionated into a gasoline, kerosene, diesel and high boiling fraction by distillation or further processed to a diesel-like fuel by catalytic co-hydrodeodeoxygenation with bio-oil.[104]

This bioCRACK oil is evaporated together with the bio-oil fraction, which is the third liquid fraction of the bioCRACK process. The dissolution of biogenic compounds into the heat carrier and the bioCRACK oil phase is the major reason for the low carbon content, the high acid content and the high water- and oxygen content of the polar aqueous bioCRACK bio-oil.

The major gas components are given in Table 6.3.

103 J. Ritzberger, P. Pucher, N. Schwaiger, and M. Siebenhofer, *Chem. Eng. Trans.*, 2014, **39**, 1189–1194.

104 H. Pucher, N. Schwaiger, R. Feiner, L. Ellmaier, P. Pucher, B. S. Chernev, and M. Siebenhofer, *Green Chem.*, 2014.

Table 6.2. Elemental composition of bioCRACK product streams

product stream	C (wt%)	H (wt%)	N (wt %)	residual (wt%)
biochar (BCH)	80.9%	5.4%	<1	13.5%
bioCRACK oil (BCO)	84.8%	12.4%	<1	2.4%
liquid heat carrier (LHC)	86.5%	12.1%	<1	0.9%

Table 6.3. Major gas components (v/v % of gas)

sample	CO (v/v %)	CO_2 (v/v %)	CO_2:CO
	43.8	44.5	1.01

Table 6.4. Bio-oil, ultimate and proximate composition (wet oil basis)

sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	ash (wt%)	H_2O (wt%)	density (g/mL)	pH
dehydrated bio-oil	50.5	7.1	0.4	41.5	0.5	9.9	1.22	2.7
bio-oil	23.2	9.4	0.3	67.1	NA	56.3	1.07	2.6
bio-oil condensate	14.4	9.97	0.3	75.3	NA	68.9	1.04	3.0

6.3.3. BIO-OIL DEHYDRATION

During short path distillation bio-oil was split in two fractions, 74 % of condensate and 22 % bottom product, latter being used for hydrodeoxygenation. 4 % of the feed were lost as light boiling fraction due to low pressure operation at 130 mbar. Table 6.4 shows the composition of the feed compared to the dehydration products (bio-oil).

6.3.4. BIO-OIL FRACTION ANALYSIS

The results of ultimate, proximate, and water by Karl-Fisher titration analysis are in Table 6.4. These analyses are of the bioCRACK bio-oil fractions as recovered from the pilot plant. The organic O contents in the bio-oils were calculated from the difference in total O (determined by difference) and O in water.

The bio-oils were analyzed at PNNL. The results are shown in Table 6.5. The C, H, O composition is calculated from wet oil composition by subtracting the amount of oxygen and hydrogen of the measured moisture content. Detailed trace element analysis of the wet bio-oils was performed by ICP. The results are shown in Table 6.6. The bio-oils are essentially mineral free, but with a

Table 6.5. Analysis of bioCRACK bio-oils

Sample name	C	H	H/C ratio	O	Moisture	N	S	Density	TAN	Viscosity
	wt% dry	wt% dry	dry basis	wt% dry	wt%	wt% wet	wt% wet	g/ml @40°C	mg KOH/g	mm²/s @40 °C
dehydrated bio-oil	59.1	6.7	1.36	33.4	10.24	0.14	0.50	1.226	135	105
bio-oil	51.1	6.2	1.45	42.6	57.43	<0.05	0.03	1.097	101	2.3

Table 6.6. Trace analysis of bioCRACK bio-oils

	S	Al	Si	K	Fe	Ca	Mg	P
dehydrated bio-oil	3372	<15	<15	24	39	17	<15	<15
bio-oil	557	<15	<15	<15	<15	<15	<15	<15

significant amount of sulfur. The TAN (total acid number) was also determined by PNNL. Viscosity and density were determined with a Stabinger viscosimeter according to ASTM D7042.

Semi-quantitative analysis of the two bioCRACK feedstocks was performed with gas chromatography-mass spectrometry (GC-MS). With the Agilent peak matching program tentative identifications were applied to the components and their relative quantities were determined based on total ion current. The results are presented in Table 6.7, showing the relative quantities of the identified components. The two bio-oil fractions show some distinct differences in composition. Overwhelmingly they contain typical fast pyrolysis bio-oil components, a mixture of guaiacols and light oxygenates.

The guaiacol (2-methoxyphenol) compounds have the typical alkyl and carbonyl substituents on the 4 position. There is a significant amount of levoglucosan in both Bio-oil fractions, but significantly lower concentration in the whole bio-oil. The bio-oil product has a large number of light oxygenates, which were not found in the dehydrated bio-oil. These compounds, e.g. acetic acid and acetol (hydroxyacetone), were separated during distillation. On the other hand the dehydrated bio-oil has a larger concentration of all the phenolic compounds, with the exception of guaiacol and methyl guaiacol.

6.3.5. HYDROPROCESSING RESULTS

For both of the reported tests the products and data were collected over the entire period with individual products and data sets collected in operating

Table 6.7. Components in bioCRACK bio-oils based on GC-MS analysis

	dehydrated bio-oil		bio-oil	
component	retention time	quantity	retention time	quantity
methyl acetate	1.756	1.3	1.737	3
formic acid		ND	1.96	0.5
acetic acid	2.37-2.49	6.8	2.7	25.9
acetol (hydroxyacetone)	2.79-3.01	3.8	2.82	21.1
propionic acid		ND	4.20-4.34	1.5
1-hydroxy-2-butanone		ND	5.10-5.16	0.3
butanedial		ND	5.74-5.90	0.4
methylene cyclopropane		ND	7.92-7.95	0.2
cyclopentenones		ND	8.00-8.10	0.2
methyl cyclopentenone		ND	10.86-10.90	0.4
γ-butyrolactone	11.64-11.77	0.4	11.34-11.44	1.3
methyl furfural		ND	12.51	0.5
3-methyl-2,5-dihydrofuran		ND	13.04	0.4
hydroxyl-me-cyclopentenone	13.79-13.91	6.1	13.71-14.02	7.5
methyl-2,3-dihydrofuran	13.92-13.96	5		ND
trans-cyclopentanediol		ND	14.05	1
guaiacol	14.63-14.65	1.2	14.56	2.4
methyl guaiacol	16.02-16.08	3.8	15.99	3.8
catechol	16.94	1.4	16.94	0.8
ethyl guaiacol	17.06	3.4	17.06	2.2
hydroxy dimethyl cyclopentenone	17.21	0.3	17.26	1.1
hydroquinone	17.76	4.1	17.81-17.92	2.8
propyl guaiacol	18.05	2.9	18.05	1.6
vanillin	18.68	6.6	18.73	2.4
methyl benzaldehyde	19.03	3.6		ND
guaiacol ethanone	19.55	4.3	19.57	1.6
guaiacol propanone	19.92	8.2	19.93	3.3
levoglucosan	20.15-20.38	35.3	20.20-20.69	13.7
ethyl homovanillate	26.54	1.4	26.58	0.3

ND = not detected

windows from 6 to 12 h long. The hydrogen consumption has been calculated and the yield of gas and oil products determined.

The dehydrated bio-oil feedstock was pumped directly into the mini-hydrotreater without pre-processing. The feedstock was assumed to have <0.1 % filterable solids content, based on BDI data provided. A fixed bed of pre-sulfided CoMo on alumina catalyst (3.5 % CoO and 14 % MoO_3) from AlfaAesar (#40435) ground to a 30-60 mesh particle size was used at standard conditions of nominally 400 °C, 12.1 mPa, and a liquid hourly space velocity of 0.2. Three

Table 6.8. Hydrotreating products from dehydrated bio-oil (elemental contents are normalized to 100%)

C content dry basis	H content dry basis	O content dry basis	H/C ratio dry basis	Density, g/ml	Moisture Content	Total Acid Number	Mass Balance	Carbon Balance
85.04	13.86	1.10	1.94	0.755	0.24	<0.01	93.6	90.6
85.55	13.24	1.21	1.84	0.784	0.26	<0.01	99.2	98.5
85.41	13.51	1.08	1.88	0.789	0.30	<0.01	92.4	88.3

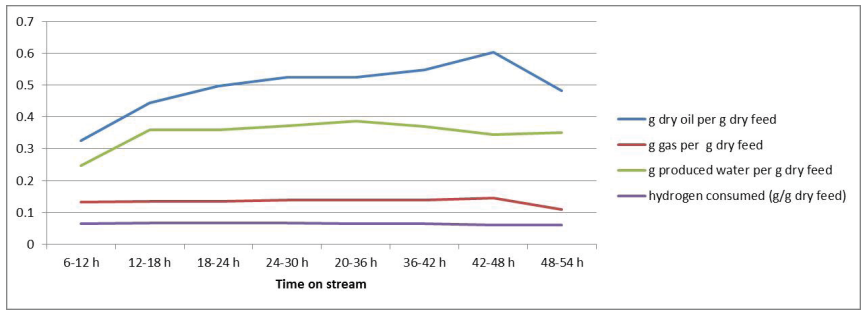


Figure 6.6. Process results from hydrotreating bioCRACK dehydrated bio-oil

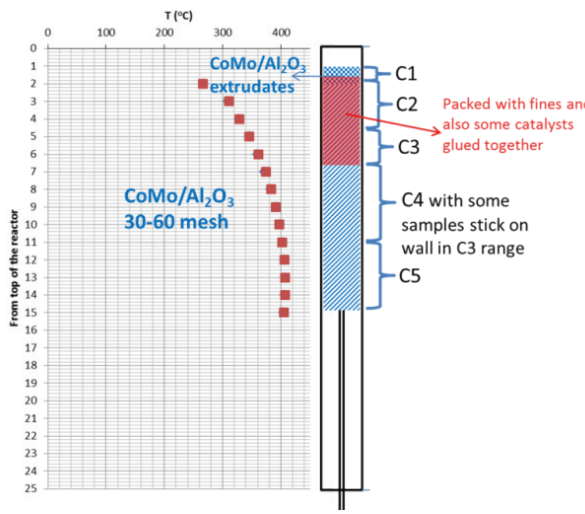


Figure 6.7. Schematic of catalytic reactor bed following test

oil samples selected to represent the product over the 54 h test were analyzed as reported in Table 6.8. Elemental contents are normalized to 100 %; S and N were <0.02 and <0.05, respectively.

Table 6.9. Products from hydrotreating bioCRACK bio-oil (elemental contents are normalized to 100 %)

C content dry basis	H content dry basis	O content dry basis	H/C ratio dry basis	Density, g/ml	Moisture Content	Total Acid Number	Mass Balance	Carbon Balance
84.30	14.96	0.74	2.11	0.712	0.36	<0.01	85.6	84.9
83.94	15.22	0.84	2.15	0.722	0.34	<0.01	85.4	81.7
84.27	14.77	0.96	2.08	0.730	0.30	<0.01	84.2	77.8
84.41	14.91	0.68	2.10	0.726	0.44	<0.01	86.5	85.2

Trace element analysis of the feedstock showed only small amounts of a few expected biomass components, 17 ppm Ca and 24 ppm K with 38 ppm Fe and 3320 ppm S. The Fe is likely a corrosion product. The high S level is unexpected. The S number for the feedstock was found by inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurement, but it is similar to that by the thermal method (0.50 wt%). Since a sulfided catalyst was used for the processing there was no conflict. In fact, we added di-tertiarybutyl-disulfide to the feedstock to maintain at least 150 ppm of sulfur.

The operating results as shown in Figure 6.6 were fairly consistent throughout the test period. The liquid oil yield from the bioCRACK dehydrated bio-oil was 0.5 to 0.6 g/g, with lower but still significant gas and water production. The hydrogen consumption was a bit higher than typically seen with fast pyrolysis bio-oil.

Gas products were analyzed through the test using gas chromatography. The gas product was composed of carbon oxides (21-26 % CO_2 and 4-5 % CO) and alkane hydrocarbon gases (22-25 % CH_4, 22-19 % C_2, 14-12 % C_3, 6-11 % C_4, 5 % C_5) diluted with the excess hydrogen (93-94 vol% of off gas).

The 316 SS tubular reactor is depicted in Figure 6.7 and the area of fouled catalyst after the test is shaded in red.

ICP analysis of the spent catalyst bed showed some evidence of deposits in the bed. As might be expected the feed contaminants, Fe, Ca, and K, were found at levels higher than in the fresh catalyst with exceptionally high levels at the point in the catalyst bed where the reactants exceeded 300 °C. Zn and Mn (below detection limit in the feed) also followed this trend, as did chromium and nickel, which are likely reactor wall corrosion products.

A similar test was performed with the bioCRACK bio-oil product. The bio-oil feedstock was pumped directly into the mini-hydrotreater without pre-processing. Four oil samples selected to represent the product over the 62 h test were analyzed as reported in Table 6.9. Elemental contents are normalized to 100 %; S and N were <0.05 and <0.05, respectively.

The operating results as shown in Figure 6.8 were fairly consistent throughout the four test periods. The liquid oil yield from the bioCRACK bio-oil was only 0.3 g per g of dry feed with significant gas and water production as well. The yield of dry oil product on a carbon basis is similar to the dehydrated bio-oil, at about 50 %. The hydrogen consumption was also high at about 7 wt% on a dry feed basis.

Gas products were analyzed through the test using gas chromatography. The gas product was composed of carbon oxides (6-9 % CO_2 and 0 % CO) and alkane hydrocarbon gases (21-17 % CH_4, 30-35 % C_2, 25-21 % C_3, 18-11 % C_4, 0-5 % C_5) diluted with the excess hydrogen (95-97 vol% of off gas).

No trace elements were detected in the bio-oil by ICP (<15 ppm) except S. There were elements found deposited onto the catalyst after the test including Si, Ca, Mg, and Na, which were likely derived from the feedstock. In addition, there were elevated levels of Fe and Cr, which could be attributed to corrosion.

6.4. *DISCUSSION*

The bioCRACK bio-oil fractions performed well for up to 62 h when using a representative hydrotreating catalyst in a single temperature stage configuration. The light oil phase product was sufficiently hydrotreated so that nitrogen and sulfur were at or below the level of detection, while the residual oxygen content was low, <1 %. The density of the products were relatively low compared to literature values for hydrotreated bio-oil, 0.71 g/mL up to 0.79 g/mL. The lighter products were produced from the bio-oil fraction which was found to contain lower molecular weight and more saturated components as fed to the hydrotreater. It is no surprise that the product from the higher molecular weight and more aromatic dehydrated bio-oil is higher in density. The dehydrated bio-oil appears to contain less reactive functional groups, which are less easily deoxygenated as shown by the difference in oxygen analysis, a reduction of 98.1 % for the bio-oil and only 96.6 % reduction in the dehydrated bio-oil. Since both bio-oil feedstocks were processed at the same space velocity, the higher oil product yield and lower gas product yield for the dehydrated product is significant. The space velocity of 0.2 used in these tests is also higher than other reports for hydrotreating bio-oil to similarly high-quality hydrocarbon products.

For the purposes of this thesis, a van Krevelen analysis has been applied to the hydrotreating products. As seen in Figure 6.9, The change in product

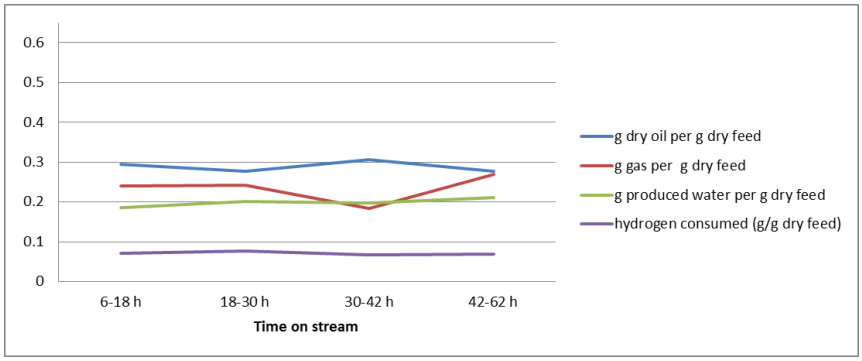


Figure 6.8. Process results from hydrotreating bioCRACK bio-oil

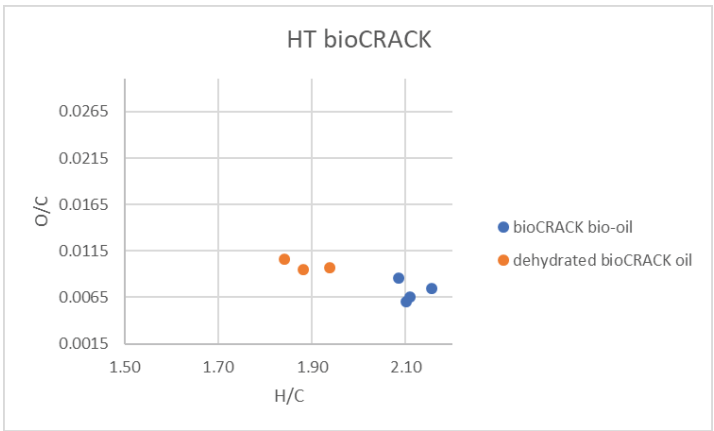


Figure 6.9. van Krevelen plot of hydrotreated products from bioCRACK oil products

compositions over the time of the experiment (62 h) is a random variation. The compositions of the bioCRACK bio-oil and the dehydrated bio-oil are unrelated to time on stream.

The consistency of the operating results and the products over the time of these experiments suggest little loss of catalyst activity through the test. The apparent drop in oil and gas production in the last data window, when feeding the dehydrated bio-oil, may be better explained as experimental variability in correction of the higher production in the previous data window. The consistency of these results contrasts with most reports in the literature for hydrotreating bio-oil.[105] Similar consistency of operation has only been achieved by

105 E. Furimsky, *Catal. Today*, 2013, **217**, 13–56.

a pretreatment of low-severity hydroprocessing prior to the actual hydrotreating.[106] In addition, a two-temperature stage hydrotreating has been used to avoid fouling of the hydrotreating catalyst bed[107] or the use of precious metal catalysts.[108]

6.5. CONCLUSIONS

With this mini-hydrotreater system we can make a preliminary assessment of the hydrotreating results with the bioCRACK feedstocks. We conclude that these feedstocks can be readily hydrotreated based on high yield of deoxygenated liquid hydrocarbon product. The results contrast with those for fast pyrolysis Bio-oil in that the catalyst bed did not foul in these extended runs and this even when using only a single temperature bed with conventional hydrotreating catalyst and without a precious metal catalyst hydroprocessing pretreatment. The tests do not represent optimized conditions, but only a first proof of principle. The oil products have been highly saturated and the hydrogen consumption could probably be reduced by changes in operating parameters such as lower operating pressure and faster throughput to reduce the residence time in the catalyst bed.

106 A. H. Zacher, M. V. Olarte, D. M. Santosa, D. C. Elliott, and S. B. Jones, *Green Chem.*, 2014, **16**, 491.

107 D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness, M. V. Olarte, A. H. Zacher, and Y. Solantausta, *Energy & Fuels*, 2012, **26**, 3891–3896.

108 J. Wildschut, F. H. Mahfud, R. H. Venderbosch, and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2009, **48**, 10324–10334.

7

Hydrotreating *In Situ* Catalytic Fast Pyrolysis Liquid Product

Agblevor, F.; Elliott, D.C.; Santosa, D.M.; Olarte, M.V.; Burton, S.; Swita, M.; Beis, S.; Christian, K.; Sargent, B. 2016. "Red Mud Catalytic Pyrolysis of Pinyon Juniper and Single Stage Hydrotreatment of Oils." **Energy & Fuels** *30*(9), 7947-7958, DOI: 10.1021/acs.energyfuels.6b00925, Publication Date (Web): July 2, 2016.

7.1. INTRODUCTION

The need to develop technical and economically viable biofuels technology is pressing need throughout the world because sustainably grown biomass can result in low carbon footprint fuel. Low carbon footprint fuels are desirable because the potential global warming trends and the need to reduce pollution from fossil fuels. The major challenges facing biofuel production are two-fold, high feedstock costs and a technical and economically viable technology that will be competitive with inexpensive fossil fuels. Biomass feedstock costs are due to low energy density, transportation costs, and sustainability challenges. The USA western states have over 20 million hectares (50 million acres) of pinyon juniper (PJ) forests.[109] These are very sparsely dispersed resources that are gradually encroaching on the grazing lands. The USA Bureau of Land Management has engaged contractors to harvest and dispose of this biomass. In the state of Utah alone, over 40,000 acres are harvested every year and disposed of through mastication because there are no viable applications for this material.[110] One potential solution to this problem is to use the biomass to produce biofuels. In our previous publication[111] we demonstrated that pinyon juniper (PJ) could be successfully pyrolyzed to produce pyrolysis oils.

Conventional fast pyrolysis of biomass can produce unstable highly oxygenated liquids that are difficult to upgrade using conventional petrochemical unit operations. However, recent advances in catalytic pyrolysis has shown that by eliminating reactive species from the oils, the stability of the oils can be improved and therefore the oils could be potentially co-processed with standard gas oils or hydrogenated for further processing to high quality biofuels which can be used alone or used as blending stock.[112,113]

One important process in pyrolysis oils upgrading is hydrogenation, which has been a major challenge because of the tendency of the pyrolysis oil to solidify and form char and coke instead of oils. This unstable property of bio-oil has been attributed to its high oxygen content. One of the viable methods developed by researchers is to subject the unstable pyrolysis oil to a mild hydrotreatment to stabilize the oil and then follow this with a more severe

109 Floyd, M.L.; Clifford, M.; Cobb, N.S.;Hanna, D.; Delph, R.; Ford, P.; Turner, D. Ecol Appl 19(5) (2009) 1223-1230.
110 Young, K.R.; Roundy, B.A.; Eggett, D.L. Appl Environ Soil Sci 2014 (2014) 1.
111 Yathavan, B.K.; Agblevor, F.A. Energy Fuels 27 (2013) 6858-6865.
112 Agblevor, F.A.; Mante, O.; McClung, R.; Oyama, S.T.; Biomass Bioenerg 45 (2012)130-137.
113 Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J., Olarte, M.V.; Zacher, A.H.; Solantausta, Y. Energ Fuels 26 (2012) 3891-3896.

hydrotreatment process to produce suitable fuels.[113] The most important catalyst used in this process has been sulfided cobalt/molybdenum oxide supported on either alumina or zirconium. This catalyst has been demonstrated to be effective for the two-stage hydrotreating of pyrolysis, where the first stage mild hydrotreatment catalyst was ruthenium on carbon.[113] However, this method has not been extensively studied for the hydrotreating of catalytic pyrolysis oils, and the question has not been answered whether there is a need for two stages in the case of catalytic pyrolysis oils as reported by Elliott et al.[114]

The most common catalyst used for the catalytic pyrolysis process has been various zeolites and their modifications. Zeolites partially deoxygenate the pyrolysis oils but they also produce coke, water and gases that reduce the yields of the organic liquid products.[115] Research into developing new catalysts that are robust, inexpensive, and will increase yields of stable pyrolysis oils is a major priority area in most laboratories throughout the world. This trend can be seen in the large number of publications using various kinds of catalyst.[116,117,118,119,120]

Red mud and other metallurgical slags are potential waste materials that could be used to produce catalysts for biomass catalytic pyrolysis. Red mud is a waste product from the Bayer process for producing alumina and is composed of a large number of metal oxides dominated by iron and aluminum oxides. We have shown that red mud can be used as an effective catalyst for biomass pyrolysis .[111] In the current studies we report the catalytic pyrolysis of JP wood and using red mud and upgrading the oils with sulfide cobalt/molybdenum oxide supported on zirconia. The ultimate objective of these studies is to develop inexpensive robust catalysts that can be used to convert low cost biomass feedstocks to stable biomass pyrolysis oils and subsequently hydrogenate them to high–energy–density biofuels.

114 Elliott, D.C.; Wang, H.; French, R.; Deutch, S.; Iisa, K. Energ Fuels 28 (2014) 5909-5917.

115 Agblevor, F.A.; Beis, S.; Masnte, O.; Abdoulmoumine, N. Ind Eng Chem Res 49 (2010) 3533-3538.

116 Mante, D.; Agblevor, F.A.; McClung, R. Biomass Convers Biorefin 1(4) (2011) 189-201.

117 Zhang, Y.; Xiao, R.; Gu, X.; Zhang, H.; Shen, D.; He, G. BioResour 9(3) (2014) 5243-5245.

118 Wan, S.; Wang, Y. Front Chem Sci Eng 8(3) (2014) 280-294.

119 Lappas, A.A.; Kalogiannis, K.G.; Iliopoulou, E.F.; Triantafyllidis, K.S.; Stefanidis, S.D. Energ Environ 1 (3) (2012) 285-297.

120 Xia, H.; Yan, X.;Xu, S.; Yang, L.;Ge, Y.; Wang, J.;Zuo, S.J. J Chem 2015 (2015) 1-11.

7.2. EXPERIMENTAL SECTION

The biomass feedstock used in these studies was PJ that was harvested by the US Bureau of Land Management contractors in Utah. The biomass consisted of wood, bark, and other residues such as leaves. The materials were not sorted prior to the pyrolysis. The harvested materials were chipped and shipped in barrels to the USTAR Bioenergy Center at Utah State University, Logan UT. The materials were further ground in Wiley mill (model 4, Thomas Scientific) to pass a 2-mm and 3-mm mesh. These samples were stored at room temperature until the time of pyrolysis. The biomass feedstock was characterized for moisture content, higher heating value (HHV), elemental composition, ash content, and thermogravimetric analysis.

The catalyst used for these studies was red mud supplied by Almatis Inc, Burnside, LA. The red mud was dried at room temperature and then ground to and sieved to particle size of 125 to 180 μm for fluidized bed pyrolysis. The ground particles were calcined at 550 °C in a muffle furnace (Thermo Fischer Scientific) for 5 h before being used for the pyrolysis. The detailed characterization of the fresh red mud and regenerated red mud have been reported by Yathavan and Agblevor . [111]

The catalytic pyrolysis of the biomass feedstocks were conducted in a 0.93 kg/h (2 lb/h) fluidized bed pyrolysis unit located at the Thermochemical Biomass Research Lab, Utah State University, UT. The details of this reactor have been reported by Mante and Agblevor.[121] The reactor consists of a 4 in schedule 10 pipe spool with a bed support and gas distributor at the bottom and a gas exhaust at the top. The reactor was externally heated to maintain an average operating temperature of 450 °C using a three-zone furnace (ATS Series 3210 Split Tube Furnace) rated for operation up to 1000 °C. The biomass feedstock was fed continuously from a gravimetric, double-screw feeder (Brabender Technologies Inc.) through a ball valve into the hot fluidized bed containing about 1.0 kg red mud catalyst. The ball valve was employed to provide a pressure seal between the feeder and the fluidized bed. For each experiment, about 5 kg of biomass was fed to achieve a catalyst-to-feed ratio of 0.20 (w/w) by the end of the run. Initially, 1.0 standard cubic feet per minute (SCFM) of nitrogen was used for fluidization and after 10 min into the run, the nitrogen gas was gradually replaced with the non-condensable

121 Mante, O.D.; Agblevor, F.A.; Green Chem 16 (2014) 3364-3377.

gases from the catalytic pyrolysis until the fluidizing gas was made up of 0.4 SCFM of nitrogen and 1.2 SCFM of syngas (75 % syngas). During the process, the mixture of char, vapors and gases that exited from the reactor was separated by a high–temperature filtration system maintained at 400 °C. The hot gas filter system consisted of a 6 in schedule 10 pipe spool with a char collection cone and gas inlet port at the bottom. The separated gases and vapors were then passed through primary and secondary tube-in-shell heat exchangers as well as a venturi scrubber to condense the pyrolysis vapors and to quench the non-condensable gases. A process water chiller unit was used to provide a cooling medium for the three stage condensing system. The primary condenser utilized an indirect cooling loop to control condenser temperature, whereas, the secondary condenser used the direct cooling of the process chiller. The aerosols that escaped the venturi scrubber were captured by a wet electrostatic precipitator (WESP) maintained at 30 kV. The non-condensable gases were further cleaned with coalescing filters before entering a syngas compressor for recycling into the pyrolysis unit. The syngas compressor provided the gas pressure necessary for recirculation of syngas for fluidization. The entire process was remotely controlled and temperatures, pressures and gas flows were all monitored by National Instrument's LabView and Fieldpoint embedded controller with input/output (I/O) modules. The evolved gases were analyzed online by a micro gas chromatography (Varian 490-GC). The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5 Å column and a 10 m porous polymer (PPU) column. Each module was equipped with a thermal conductivity detector. The MS column was used to analyze H_2, CH_4 and CO. CO_2 and C_1-C_4 gases were analyzed by the PPU column. The yields of the products were determined gravimetrically and the mass of char/coke was determined by weighing the hot gas filter collection canister and the reactor content before and after each pyrolysis experiment. The total mass of bio-oil was measured by weighing the condensers and electrostatic precipitator reservoirs before and after each experiment. The total mass of the non-condensable gas was determined by difference and by calculation from GC analysis.

During the run, samples of pyrolysis oils were collected every hour from the ESP and used to determine the viscosities, densities, and pH values of the oils. The hourly viscosity data were used to monitor the activity of the catalyst and to determine the end of each run. When the viscosities were too high (>100 cP) the run was stopped and the catalyst regenerated in a muffle

furnace at 550 °C for 5 h and then fed back into the reactor the next run. Makeup catalysts (1 wt %) were added to the red mud after each run. During this campaign, a total organic liquid of more than 1 L was the target. Thus, there were five total runs to produce more than 1 L of organic fraction for characterization and hydrotreating studies.

The bio-oils collected on hourly basis and the composite oils after a complete run of 5 h from the catalytic pyrolysis experiment were characterized for the following properties. The acidity was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 5-10 min stabilization of the mechanically stirred oil. The viscosity of the bio-oils was measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were equivalent to viscosities determined by ASTM D445 method. The stability of the bio-oils was measured as a change in viscosity during storage at room temperatures. The bio-oils used for the studies were stored in a 100 mL air-tight glass vials sealed with a plastic cap under laboratory ambient conditions for a minimum of 12 months. Their viscosities were taken at various time periods during the storage. The SVM 3000 Stabinger viscometer was also used to measure the densities of the oils. Calibrations were done prior to measurements with distilled water free from bubbles. A Metrohm 701 KF Titrino (Metrohm Instruments, Riverview, FL) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal composite 5 reagent was used. 50 mL of methanol were placed in the titration vessel and conditioned. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded.

The elemental compositions of the pyrolysis oils were determined using Thermo Fischer Flash 2000 CHNS/O organic elemental analyzer (Thermo Fischer Scientific. Inc, Waltham, MA). About 10 mg of sample was used for each analysis. The higher heating value (HHV) of the samples were determined using the IKA basic bomb calorimeter (IKA Works Inc, Wilmington, NC). The volatile matter, fixed carbon, and thermogravimetic analysis were determined using TA Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE). The total acid number (TAN) of the composite oils and hourly samples were also determined by ALS (ALS Environmental Laboratory, Tucson, AZ).

^{13}C nuclear magnetic resonance (NMR) spectra were collected using a 500 MHz Agilent DD2 spectrometer with a 5 mm Agilent OneNMR probe.

A single pulse sequence used a 45° pulse on carbon with 1H decoupling during acquisition (1 s). A 10 s recycle delay was used between pulses, and 4000 scans were collected for each sample. The bio-oil samples were prepared with deuterated dimethyl sulfoxide. The relaxant used was 0.05 M $Cr(acac)_3$. An inverse-gated decouopling protocol was used. The spectra were referenced to the solventand integrated to obtain carbon mole fractions of the functional groups. Mnova version 9 was used to process the data. Ablative baseline correction and manual phase adjustment were used in processing the spectra.

The catalytic pyrolysis oil samples produced at Utah State University from PJ were shipped to Pacific Northwest National Laboratory (PNNL) for hydrotreatment. The oil was hydroprocessed in the mini-hydrotreater (Figure 7.1). The hydrotreater was configured as a single pass, co-current, continuous, down-flow reactor. The system can operate at up to 12.4 MPa (1800 psig) with a maximum catalyst temperature 400 °C. It is described in detail by Elliott et al.[122]

The mini-scale hydrotreaters (30 mL fixed bed) were built for bio-oil upgrading by catalytic hydroprocessing. Tests with the catalytic pyrolysis bio-oil were completed with sulfided catalysts as shown in Table 7.1.

Campaigns were performed over the course of a 5 day test, and the products and feed were collected to assess performance. The liquid hourly space velocity (LHSV) used in these studies was liters of catalytic pyrolysis bio-oil feed per liter of catalyst bed per hour. The LHSV was increased from 0.13 to 0.15 after 176 h time on stream. For the reported test, the products and data were collected over the entire period with individual products and data sets collected in operating windows from 12 to 13 h long. The hydrogen consumption has been calculated and the yield of gas and oil products determined.

The catalyst bed was sulfided *in situ*. The reactor tube containing the catalyst was heated to 150 °C in H_2 flow, heated from 150 °C to 350 °C over 3 h in flow of H_2 and sulfiding agent (35 % di-tertiarybutyl-disulfide (DTBDS) in decane), and then heated to 400 °C and held for 5 h with H_2 and sulfiding agent flowing. For the hydroprocessing tests the flow ratio of H_2/liquid was 2500 L H_2 (L bio-oil)$^{-1}$. The operating pressure was typically 12 MPa (1780 psi). Hydrogen consumption was calculated by difference between hydrogen fed to the reactor and the hydrogen recovered in the gas product. When using the sulfided catalyst, DTBDS was added to the catalytic pyrolysis bio-oil at an

122 Elliott, D.C.; Wang, H.; Rover, M.R.; Whitmer, L.; Smith, R.; Brown, R.C. 2015. "Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover." ACS Sustain Chem Eng 3 (2015) 892-902, DOI:10.1021/ acssuschemeng.5b00015

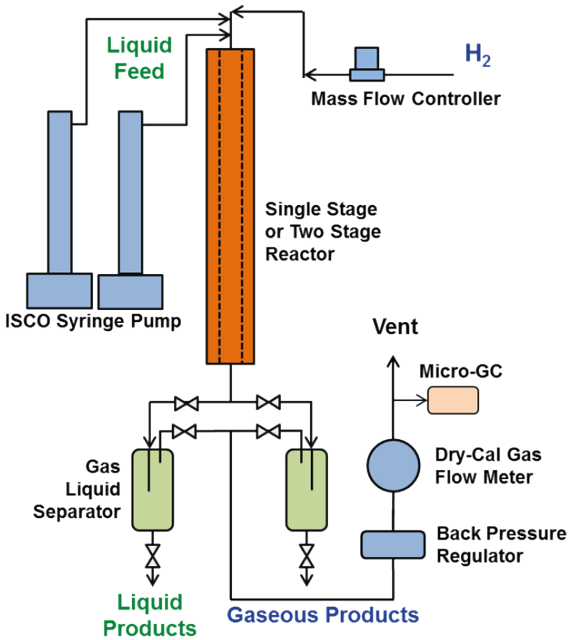


Figure 7.1. Schematic of the mini-reactor hydrotreater system

Table 7.1. Summary of Hydrotreater Test Parameters with PJ Catalytic Pyrolysis Bio-oil

Temperature, °C	400
Pressure, psig	1780
LHSV, L/L/h	0.13-0.15
H_2/bio-oil, L/L	2550
Time on stream	176-307 h
Catalyst	CoMoS*
Bed volume, mL	19

*PNNL 61176-126-1; 1.5% CoO, 6%MoO_3 on zirconia, ground to 30-60 mesh

amount equal to 150 ppm S. Figure 7.2 shows a schematic of the catalyst beds with a super-imposed temperature profile for the single stage testing mode. The temperatures were measured at the center line of the catalyst bed by a thermocouple, which was adjustable within a full length thermowell. The isothermal portions of the catalyst bed clearly show that the majority of the bed was at set-point reaction temperature (between 380 and 400 °C), and the overall lengths of the catalyst bed were used to calculate the space velocity.

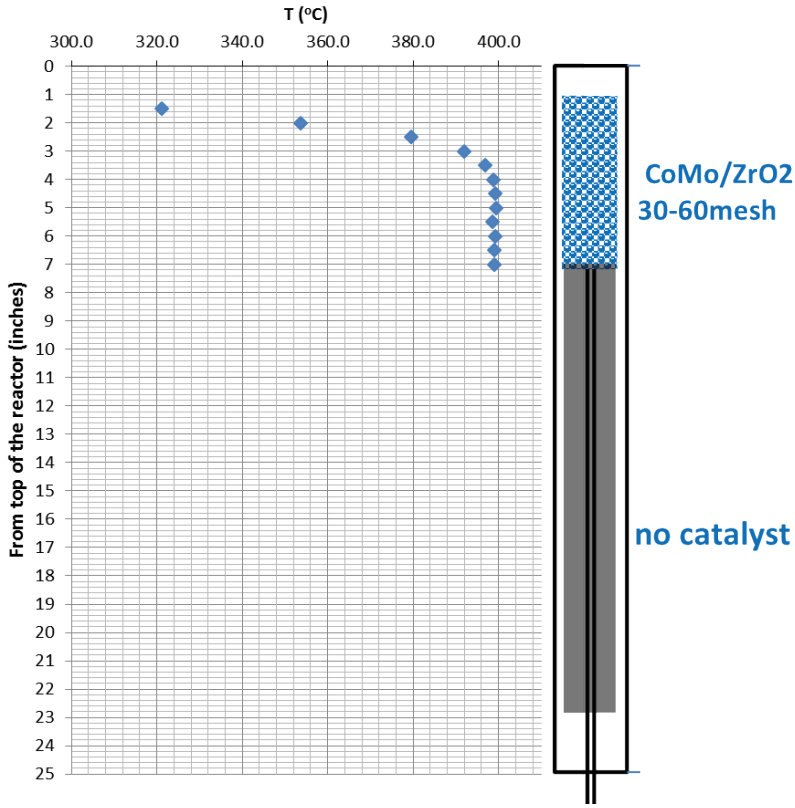


Figure 7.2. Schematic of the catalyst bed in the mini-hydrotreater reactor

7.3. RESULTS AND DISCUSSIONS

All the pinyon juniper biomass feedstock used for the catalytic pyrolysis was ground to pass through a 2 mm mesh, and the composition is shown in Table 7.2. The ultimate composition was similar to those reported by Yathavan and Agblevor.[111] The HHV was similar to those reported for other biomass feedstocks[123].

The product yield distribution of the red mud catalytic pyrolysis of the PJ is shown in Table 7.3. The runs were reproducible, and the average of several runs is shown in Table 7.3, with the standard deviations of repeated runs shown as error bars. Most of the aqueous phase produced was collected in the condensers

123 Vassilev, S.V.; Baxter, D.; Andersen D.K.; Vassileva, C.G. Fuel, 2010, 89(5), 913-933.

Table 7.2. Ultimate composition and HHV of PJ wood

parameter	composition
moisture (wt %)	9.13±0.06
ash (wt%)	1.02±0.11
carbon (wt%)	49.48±0.55
hydrogen (wt%)	6.61±0.09
nitrogen (wt%)	0.23±0.03
sulfur (wt%)	bd[a]
oxygen (wt%)	42.66±0.17
HHV (MJ/kg)	19.25±0.36

[a] bd=below detection limit

Table 7.3. Product yield distribution of red mud catalytic pyrolysis oil and pyrolysis gas composition[a]

	total liquid (wt %)	char (wt %)	gas (wt %)	pH of ESP oil	oil HHV (MJ/kg)	
composite run	43.53±2.19	24.07±3.28	32.42±3.76	3.37±0.33	27.64	
pyrolysis gas composition (mol %) on a nitrogen-free basis						
component	CO	CO_2	CH_4	H_2	C_4H_8	C_2-C_4
content (mol %)	14.10±2.20	27.17±1.53	63.67±0.60	7.76±1.93	11.20±2.81	36.03

[a] error bars are standard deviations of multiple runs

where the product formed two phases and could be easily separated. The organic fraction was separated and added to the ESP oil because the composition of the organic fraction from the condensers was found to be the same as the oils collected from the ESP. The water content of the condenser oil ranged from 50 to 60 wt%. In contrast Karl-Fischer moisture content of the ESP oil ranged from 2 to 4 wt% because most of the moisture had already been removed by the condensers. The catalytic pyrolysis gas composition is also shown in Table 7.3 on nitrogen-free basis. Although the carbon dioxide content was relatively high, significant amount of hydrocarbon gases were also produced in addition to the hydrogen produced from the water-gas shift reaction promoted by the iron in the red mud. Thus the pyrolysis gases were relatively rich in hydrogen and could be potentially used to heat the pyrolysis reactor. A fraction of the gases (75 %) was recycled to fluidize the bed material and the rest was flared.

The progress of the red mud catalytic pyrolysis of PJ was monitored by measuring the viscosity of the oil collected in the electrostatic precipitator (ESP)

with time on stream. Figure 7.3 clearly showed that as time on stream increased the viscosity of the oil increased and this was attributed to the partial deactivation of the red mud catalyst. The deoxygenation of the oil decreased and the density of the oil also increased. Yathavan and Agblevor[111] also observed that the viscosity of pinyon juniper bio-oil pyrolyzed on sand was almost 6 times that pyrolyzed on red mud and three times that pyrolyzed using HZSM-5 zeolite. When the red mud was partially deactivated the viscosity of the oil increased, but when it was regenerated by burning off the coke at 575 °C for five hours, the viscosity of the oil produced using the regenerated red mud was similar to that produced using the fresh red mud. These observations clearly showed that the increase in viscosity was due to the deactivation of the red mud catalyst. The increasing trend in viscosity with time on stream was corroborated with the ^{13}C NMR and elemental analysis data discussed below.

The reaction progress was also monitored by gas compositional analysis by taking ratios of CO to CO_2 over time. As reported in Yathavan and Agblevor,[111] the CO_2 content was relatively higher than those observed for the HZSM-5 catalytic pyrolysis because of water gas shift reaction. The variation in the gas composition is shown in Figure 7.4. After the first 80 min the CO/CO_2 ratio appeared to achieve a steady state and increased only slightly for the rest of the time on stream. There appeared to be no correlation between the changes in viscosity of the oils and the variation in the CO/CO_2 ratio. The steady state was achieved because there was recycling of the non-condensable gases into the reactor for fluidization of the catalysts. Because of this recycling, the CO/CO_2 was not a good indicator of the activity of the red mud catalytic during the pyrolysis. Detailed characterization of red mud before and after partial deactivation during pyrolysis have been reported in Yathavan and Agblevor.[111] The response observed in the current studies were similar those observed in the above publication especially when compared to HZSM-5.

The ultimate composition, Karl Fischer moisture content and the Total Acid Number (TAN) of the hourly oils samples and the composite oil used for the hydrotreating experiments are shown in Table 7.4.

The elemental composition of the composite oil (dry basis) and acid number values are within the range of values reported for the timed samples. However, water content of the composite oil was higher than the timed samples because the composite samples included condenser oils, which normally have higher moisture content than the electrostatic precipitator oils. All time samples were taken from the electrostatic precipitator because our analysis

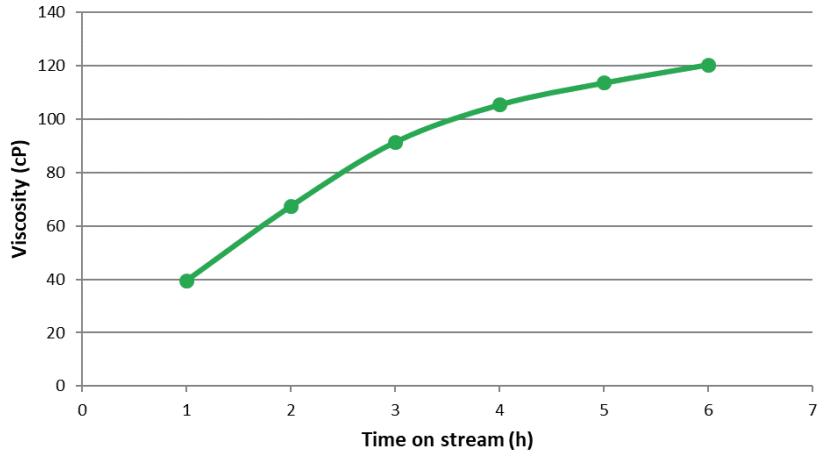


Figure 7.3. Variation of red mud catalytic pyrolysis oil viscosity with time on stream

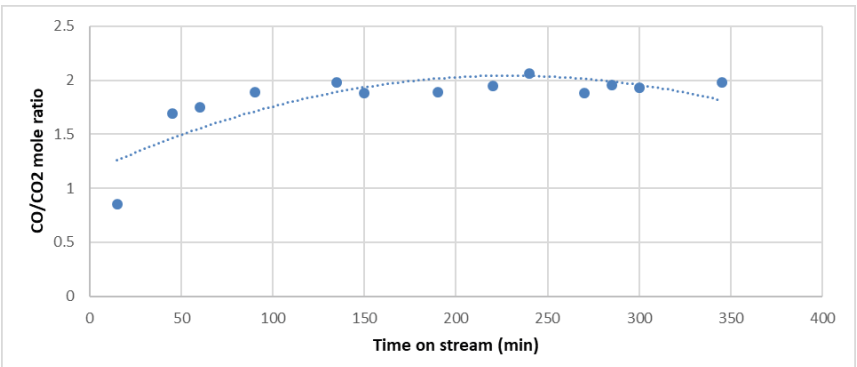


Figure 7.4. Variation of CO and CO_2 with time on stream during red mud catalytic pyrolysis of PJ.

Table 7.4. Characterization of red mud catalytic pyrolysis oils

sample	C (wt %, dry basis)	H (wt %, dry basis)	N (wt %, dry basis)	O (by difference)	S (wt %, dry basis)	water by Karl Fischer (wt %)	TAN (mg KOH/g
1H-PJ-RMAL	74.4	7.1	0.4	19.9	<0.04	2.82	56.48
2H-PJ-RMAL	72.4	7.2	0.4	21.7	<0.04	2.93	61.34
3H-PJ-RMAL	70.5	6.8	0.3	23.3	<0.1	3.52	67.52
4H-PJ-RMAL	69.6	7.1	0.3	24.7	<0.1	2.82	63.00
5H-PJ-RMAL	68.4	6.7	0.4	25.5	<0.04	3.55	65.86
composite bio-oil	70.2	6.9	0.4	22.5	<0.04	4.49	65.99

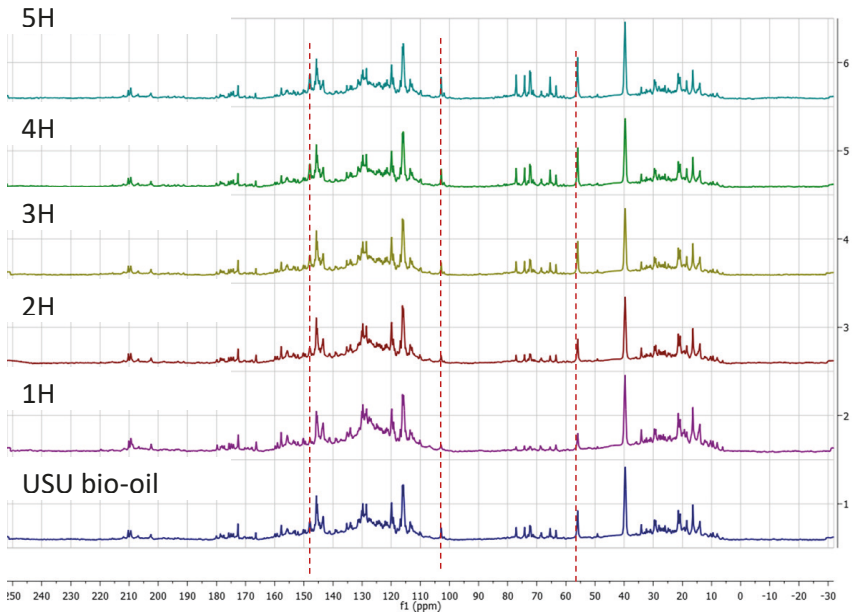


Figure 7.5. ^{13}C NMR of catalytic pyrolysis oil of PJ wood (USU bio-oil = composite oil).

Table 7.5. Distribution of various C-containing functional groups by mole percentage

sample	carbon mole fraction of functional groups in the sample (mol % C)					
	carbonyl (225-200 ppm)	carboxy (185-170 ppm)	phenolic (170-142 ppm)	aromatic/alkene (142-95 ppm)	ether/alcohol (95-45 ppm)	aliphatic (35-0 ppm)
1H-PJ-RMAL	3.94	2.79	15.4	46.2	6.6	25.2
2H-PJ-RMAL	3.18	2.63	17.9	46.2	8.8	21.3
3H-PJ-RMAL	4.04	2.49	17.6	43.1	11.5	21.3
4H-PJ-RMAL	3.49	2.89	17.3	44.3	11.9	20.2
5H-PJ-RMAL	4.43	2.35	16.7	43.0	13.0	20.5
USU bio-oil (composite oil)	3.36	2.71	17.5	43.7	10.7	22.0

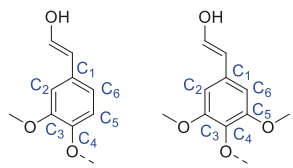


Figure 7.6. Lignin-derived structures: coniferyl- and syringyl-type structures

of the organic fraction from the condensers did not show any difference in chemical properties from the ESP oils and the ESP oils were easier to collect and analyze. The hourly samples showed that as time on stream increased, carbon content (dry basis) decreased with an increase in the oxygen content (dry basis). A general trend of an increasing acid number was also observed for the 3H sample (3H-PJ-RMAL).

The comparison of the stacked ^{13}C NMR spectra of the composite oil and timed samples is shown in Figure 7.5, with the integration shown in Table 7.5. The dotted lines in Figure 7.5 highlight some peaks that showed changes with timed samples. These peaks are typically associated with the presence of heteroatoms such as oxygen.

The 56 ppm signals are due to carbons associated with the methoxy group ($-OCH_3$) and 148 ppm is associated with aromatic carbon having an oxygen attached to it (C_3 and C_4 in coniferyl alcohol type structure and C_3 and C_5 in syringyl alcohol type structures, Figure 7.6). The peak at 103 ppm has been associated with C_2 and C_6 aromatic carbon in syringyl-type lignin structures.[124] Since the source of the oil was from pinyon juniper, which is softwood, it was expected that lignin-derived structures will be mostly coniferyl-type lignin and minimal amounts of the syringyl-type. In coniferyl alcohol moieties, C_2 peak is around 110-112 ppm while C_6 peak is around 118-120 ppm which can be clearly observed in Figure 7.5. The syringyl peaks are relatively strong suggesting that there could have been contamination from hardwood species since the PJ is essentially a forest residue due to the method of harvest.

Table 7.5 shows the integration results of the different functional groups (the detailed method of integration of the spectra included in the supplementary data). From the calculated mole fraction for each group, both aromatic carbon and aliphatic carbon groups seem to decrease as time on stream increased as also evidenced by peaks at 58-87 ppm in Figure 7.5. The trend in the data suggested that catalyst was undergoing deactivation. At the first hour (1H) when the catalyst was most active, the aromatic/alkenes region was more intense due to formation of more aromatic compounds from some of the carbohydrate decomposition compounds,[115,125] but as the catalyst deactivated this reaction slowed down and there was reduced amount of these compounds. Another

124 Ralph, S.; Landucci, L.; Ralph, J. NMR database of lignin and cell wall model compounds, US Forest Products Laboratory, One Gifford Pinchot Dr, Madison WI,(http://ars.usda.gov/Services/docs.htm?docid=10491) (accessed: January 2009), 2004.

125 Atadana, F. 2010, MS Thesis, Virginia Tech, VA

contributory factor was the demethoxylation of the lignin C9-unit; it has been reported that when the catalyst is fresh and most active, there is considerable demethoxylation of the coniferyl group,[111] but as the time on stream increased there was less demethoxylation reaction. The ether and alcohol groups increased as time on stream increased while trends for carbonyl, carboxyl, and phenolic groups were not conclusive. Comparing the trend in oxygen content of the timed samples, the increase in ether and alcohol contents seem to be the main driver for the increase in oxygen content of the oil. There appeared to be a linear correlation between the alcohol/ether carbons and the aliphatic carbons. As the ether/alcohol content decreased the aliphatic content increased which clearly suggested deoxygenation of the alcohols to produce aliphatic groups but this reaction decreased with time when the catalyst activity was reduced.

^{31}P NMR determination of –OH groups have been used in both coal and lignin applications. Recently, it was part of an inter-laboratory validation in a PNNL-NREL collaborative project on characterization of bio-oils. A phosphitylating agent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was added to the bio-oil dissolved in both deuterated and regular solvents ($CDCl_3$ and pyridine, respectively). A relaxant, chromium (III) acetyl acetonate was used to ensure complete relaxation of the ^{31}P nuclei. Ranges of interest were aliphatic OH: 145 – 152 ppm, phenolic OH: 138 – 145 ppm, carboxylic acid OH: 134.6 – 138 ppm.

The composite bio-oil and all of the five timed samples were phosphitylated. A stack plot of the resulting spectra is shown in Figure 7.7 and the quantification of the aliphatic, phenolic and carboxylic –OH groups is reported in Table 7.6. The aliphatic hydroxyl groups (mainly alcohols) content increased with the reaction time on stream (Figure 7.8). This finding corroborates the earlier insight gained through ^{13}C NMR and elemental analysis. On the other hand, there was no obvious trend in the variation of both the phenolic and carboxylic hydroxyl groups.

7.3.1. CORRELATION BETWEEN PHYSICAL PROPERTIES AND FUNCTIONAL GROUPS

Both the ^{13}C NMR and ^{31}P NMR provide quantitative analysis of some of the major functional groups in the catalytic pyrolysis oils and when these data were combined with the variation in physical properties such as viscosity, very interesting results were obtained as shown Figure 7.8, Figure 7.9, and Figure 7.10. The evolution of the viscosity, aliphatic, and ether/alcohol functional

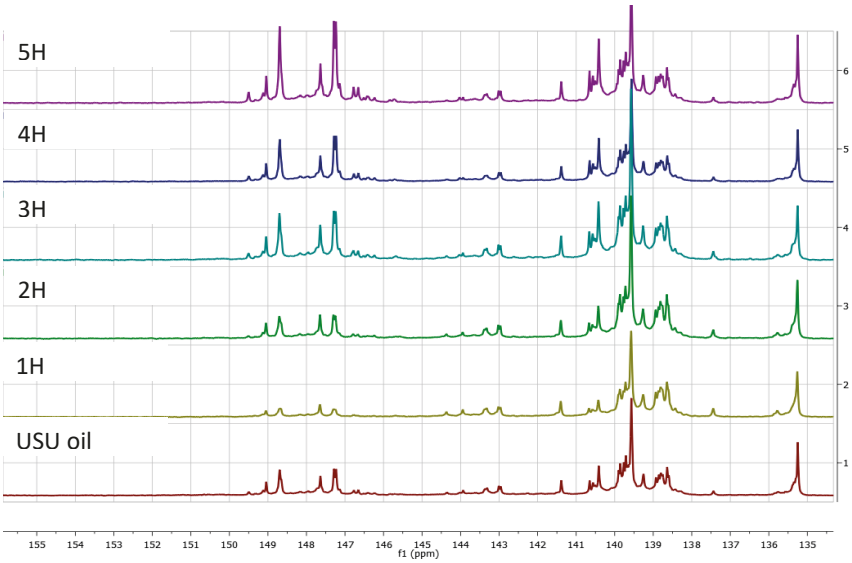


Figure 7.7. Stack plot of ^{31}P NMR spectra of catalytic pyrolysis oil sample

Table 7.6. ^{31}P NMR Quantification of hydroxyl groups present in the catalytic pyrolysis oils

	hydroxyl concentration (mmol of OH/g of bio-oil)		
sample	aliphatic (145-152 ppm)	phenolic (138-145 ppm)	carboxylic (134.6-138 ppm)
USU bio-oil (composite oil)	1.7	4.4	0.7
1H-PJ-RMAL	0.7	3.9	0.7
2H-PJ-RMAL	1.2	4.2	0.6
3H-PJ-RMAL	1.6	4.2	0.5
4H-PJ-RMAL	2.1	4.3	0.7
5H-PJ-RMAL	2.5	4.3	0.7

groups are shown in Figure 7.8. The functional groups content of the oils increased with increased time on stream and the viscosity also increased with increased time on stream. The variation in the viscosity of the catalytic pyrolysis oil with time on stream showed very strong linear correlation with the alcohol/ether content of the oils ($r^2 = 0.987$, Figure 7.9). As the alcohol/ether carbon content increased because of the decrease in the activity of the red mud catalyst, the viscosity of the oil increased almost linearly. This suggested that the function of the catalyst responsible for the breakage of the alcohol/ether bonds is the key to the reduction in the viscosity of the oils and therefore its potential stability. The aging rate of the red mud catalytic

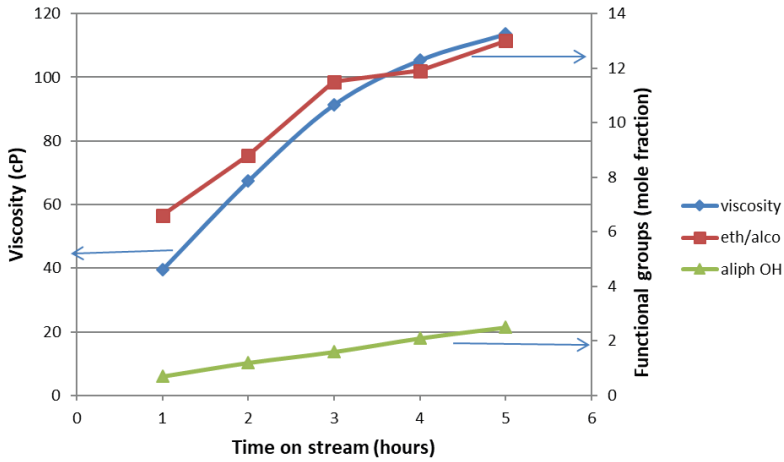


Figure 7.8. Variation of viscosity, aliphatic OH and ether/alcohol functional groups with catalytic pyrolysis time on stream (eth/alco = ether/alcohol functional groups; aliph OH = aliphatic OH)

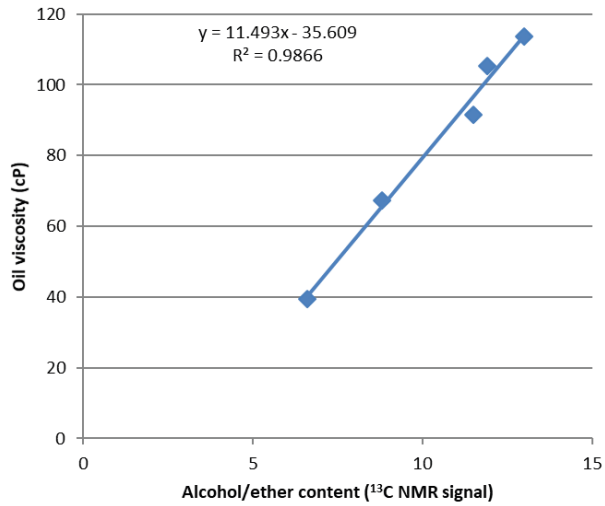


Figure 7.9. The effect of combined alcohol/ether content on the viscosity of catalytic pyrolysis oils.

pyrolysis oil is also a linear function of the time on stream. Samples collected during second hour and third hour of pyrolysis on stream had a lower aging rate of 0.120 cSt/day compared to the samples collected during the fourth hour of pyrolysis (0.225 cSt/day).[126] Thus, the alcohol/ether content of the

126 Agblevor, F.A. Whittle, J.; Akude, A.M.; Elliott, D.C.; Santosa, D.M.; Paasikallio, V. TCBiomass2015, Chicago IL, November 1-5, 2015; www.gastechnology.org/agblevor_foster_presentation

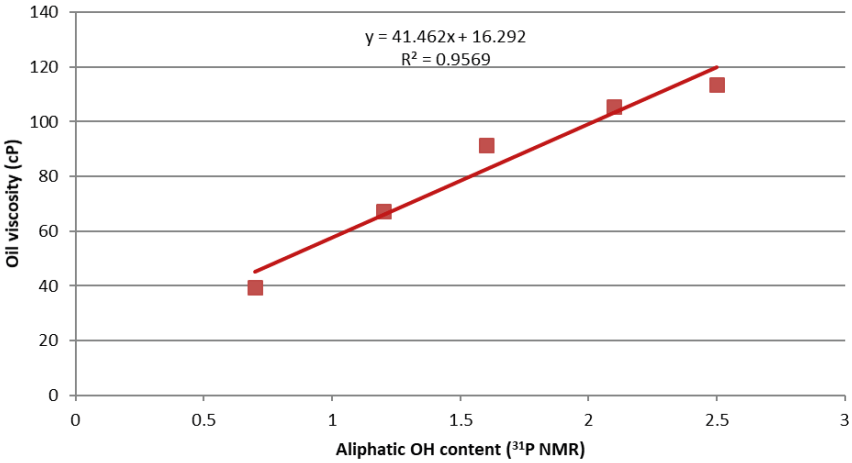


Figure 7.10. The effect of aliphatic OH content on the viscosity of the catalytic pyrolysis oils

catalytic pyrolysis oil appears to play major roles in the aging and increase in viscosity of the oils.

Further analysis of the functional groups using ^{31}P NMR also revealed that carboxylic and phenolic OH functional groups played minor roles in the viscosity evolution of the oils. In contrast the aliphatic OH group (mostly alcohols) showed relatively strong linear correlation ($r^2 = 0.957$, Figure 7.10) with the viscosity of the oils suggesting that this is also an important functional group responsible for oil aging and viscosity increases. The linear coefficient of determination for the aliphatic OH with the oil viscosity was slightly lower ($r^2 = 0.957$) than the combined alcohols and ether groups suggesting that the ether groups also play some role in the viscosity of the oils.

The trends observed in the ether/alcohol functional groups variation with viscosity is also shown in Figure 7.5, where the peaks in ether/alcohol region (58-87 ppm) of the ^{13}C NMR spectra increased in intensity with increased time on stream. Mante and Agblevor[121] also observed correlations between the viscosity of the catalytic pyrolysis oils and the C-C bonds as well as correlation between the levoglucosan content and the increase in the density of the oils. Improved stability of catalytic pyrolysis oils and decrease in viscosity with corresponding decrease in the aliphatic alcohol region (levoglucosan) content of the oil was also reported by Agblevor et al, 2010,[127] and Agblevor et al.[128]

127 Agblevor F, Mante O, Abdoulmoumine, McClung, R. *Energy & Fuels, 2010,* 24,4087-4089.
128 Agblevor, F., Beis S., Mante, O., Abdoulmoumine, N. *Ind. Eng. Chem. Res.*, 2010, 49, 3533-3538.

Table 7.7. Results from hydroprocessing catalytic pyrolysis bio-oil[a]

Product sample	H/C	O	TAN	H_2 g/g of oil	mass balance, %
TOS 19-31 h[b]	1.91	1.16	<0.01	0.074	98.9%
TOS 105-115 h[b]	1.85	1.00	<0.01	0.071	106.0%
TOS 164-176 h[b]	1.83	1.21	<0.01	0.067	102.7%
TOS 236-248 h[c]	1.82	1.13	<0.01	0.073	103.2%
TOS 297-307 h[c]	1.81	1.01	<0.01	0.070	104.5%

[a] For comparative data for non-catalytic bio-oil from pine, see the study by Elliott et al.[113]
[b] low LHSV 0.13 L $L^{-1}h^{-1}$
[c] high LHSV 0.15 L $L^{-1}h^{-1}$

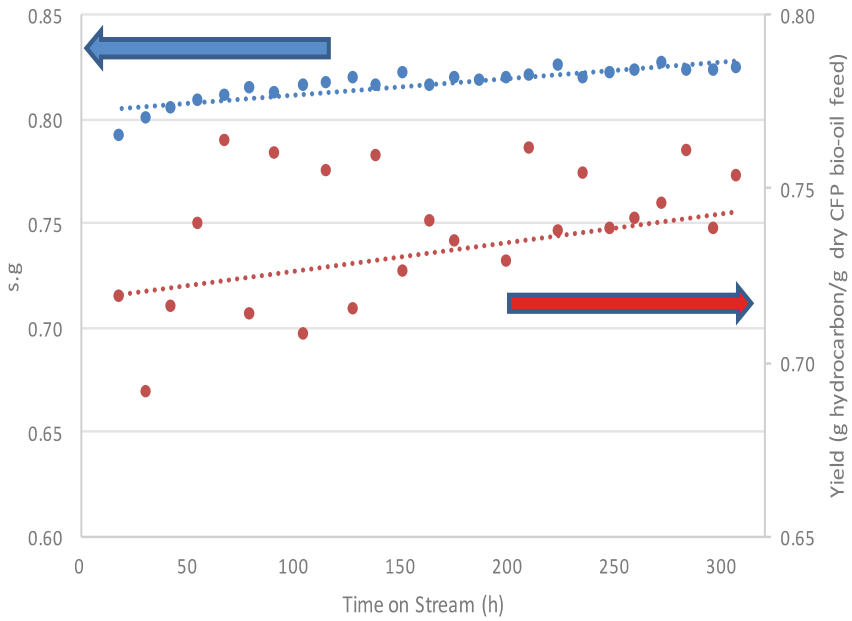


Figure 7.11. Processing Results -- Red Mud Catalyzed feedstock

The reported data learn credence to the ether/alcohol correlation with the viscosity of the bio-oils. Lignin and levoglucosan oligomers can undergo association reactions to increase viscosity of bio-oils as reported by Fratini, et al.,[129] thus it appears that this was probably the phenomenon taking place in this

129 Fratini, E.; Bonini, M.; Oasmaa, A.; Solantausta, Y.; Teixeira, J.; Baglioni, P. Langmuir, 2006, 22(1), 306-312.

process. Furthermore, levoglucosan is a solid at room temperature, and since the levoglucosan concentration appeared to increase with time on stream, it follows that the viscosity of the oil will increase and this was observed in this process and which was also reflected in the increase in the ether/alcohol contents of the bio-oils.

7.3.2. HYDROTREATMENT OF PYROLYSIS OILS

The PJ red mud catalytic pyrolysis oils received from Utah State were hydrotreated in a continuous fixed bed of sulfided $CoMo/ZrO_2$. During the upgrading of the catalytic pyrolysis oil using the sulfided catalyst, the typical catalyst bed fouling observed with fast pyrolysis bio-oil was not found with this oil. Use of the higher space velocity in the second part of the test proceeded without complication. The examination of the typical catalyst bed following an experimental run with catalytic pyrolysis bio-oil had no evidence of either cross-linked polymer or carbonaceous particulate deposit on the packing. The catalyst beds were free flowing and easily removed from the reactor tube for analysis.

Mass balances for catalytic pyrolysis bio-oil runs ranged from 87 to 108 % for the steady-state windows calculated, with carbon balances somewhat similar, ranging from 96 to 106 %. Since the liquid and gaseous products were all measured, the carbon loss can be attributed to experimental error and to residuals on the catalyst particles. The process results for hydrotreating are shown in Table 7.7. The hydrogen consumption values are somewhat higher than expected for bio-oil hydrotreating. The somewhat higher numbers for the test can be explained by the more complete saturation resulting in higher H/C ratio and density reduction.

The product yield was much higher from catalytic pyrolysis bio-oil than from the two stage hydrotreating of non-catalytic bio-oil.[113] As shown in Figure 7.11, the mass yield of hydrocarbon oil product remained high throughout the test. The comparative number for the two stage hydrotreating of non-catalytic bio-oil is about 0.4 to 0.45 as reported in Elliott, et al.[113] In this current test the mass oil yield trended to higher throughout. The density also showed an initial period of increase (suggesting catalyst break-in followed by fairly steady data after the first 75 h.

The elemental composition of the products from the catalytic pyrolysis bio-oil hydrotreating tests are shown in Table 7.8. These catalytic hydroprocessing experiments produced highly deoxygenated products but required long processing residence times resulting in low processing space velocities. The

Table 7.8. Hydrotreater feed and product analyses (dry basis)[a]

	C (wt %) D5291/ D5373	H (wt%) D5291/ D5373	Ob (wt%) D5373 (modified)	H/C	N (wt%) D5291/ D5373	S (wt%) D1552/ D4239	moisture (wt%) D6869	density g/ml @ 25 °C
Feed bio-oil	67.92	7.06	24.80	1.24	0.23	0.01	3.50	1.132
Products								
TOS 19-31h[c]	85.16	13.67	1.16	1.91	<0.05	0.02	0	0.799
TOS 105-115h[c]	85.65	13.35	1.00	1.85	<0.05	<0.01	0	0.817
TOS 164-176h[c]	85.60	13.19	1.21	1.83	<0.05	<0.01	0	0.819
TOS 236-248h[d]	85.71	13.16	1.13	1.82	<0.05	<0.01	0	0.821
TOS 297-307h[d]	85.92	13.07	1.01	1.81	<0.05	<0.01	0	0.823

[a] for comparative data for non-catalytic bio-oil from pine, see the study by Elliott et al.[113]
[b] oxygen by difference
[c] low LHSV 0.13 L $L^{-1}h^{-1}$
[d] high LHSV 0.15 L $L^{-1}h^{-1}$

sulfided CoMo catalyst was effective in hydrodeoxygenation. Hydrotreating of the nitrogen component of the catalytic pyrolysis oil was also effective, being reduced below the level of detection of the instrument. The sulfur level which was quite low in the feed catalytic pyrolysis bio-oil, was reduced below the detection level of the instrument during the hydrotreatment above 31 h when the hydrotreating catalysts bed had stabilized.

The yield of hydrocarbon liquids, when normalized for the deficient carbon balance, ranged from 0.87 to 0.96 g C/(g C in feed). These numbers are higher than those reported for the two-stage hydrotreating of non-catalytic bio-oil,[113] where the results were about 0.82, and the catalyst bed was fouled compared to the catalytic pyrolysis oils which appeared to have almost perfect non-fouled hydrotreating catalyst bed.

The hydrotreated products from catalytic pyrolysis bio-oil were also analyzed by gas chromatography simulated distillation (SimDist ASTM D2887). This method is standardized for analysis of diesel fuels, so its application to these products, which are more comparable to sweet crude, shows the important difference in the low temperature distillate range. As shown in Figure 7.12, there was a significant portion of the hydrotreated products that fell in the gasoline range. There was a small tail in each product that fell into the distillation range of heavy oil, which was similar to those found in standard diesel fuel. As shown in Table 7.9, the products were all similar but showed a slight trend toward heavier products above the 307 h period of the test, but the shift appeared mostly between the first and second products with little change

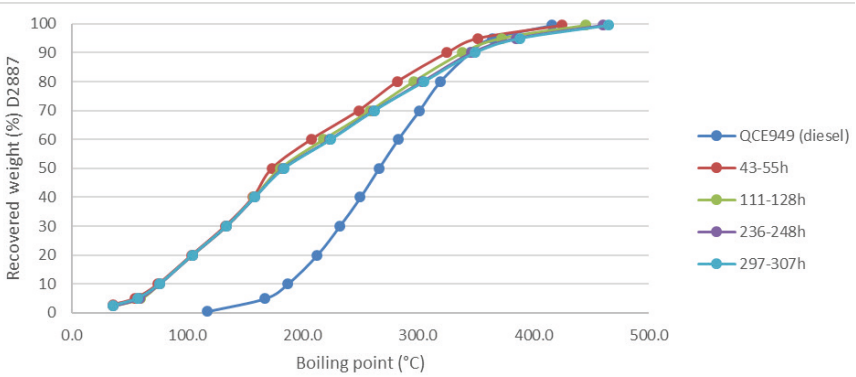


Figure 7.12. SimDist of hydrotreated catalytic pyrolysis bio-oil

Table 7.9. Quantitative data from SimDist

	ASTM D2887 -- wt%				
Fraction	QCE949 (diesel)	HT red mud 43-55h	HT red mud 111-128h	HT red mud 236-248h	HT red mud 297-307h
Gasoline (IBP-184°C)	8.9	52.5	50.4	49.7	49.5
Diesel (184-344°C)	81.5	40.8	40.7	40.1	39.9
Heavy oil (>344°C)	9.6	6.7	8.8	10.2	10.6
Jet A (153-256°C)	41.0	31.2	29.2	28.4	28.3

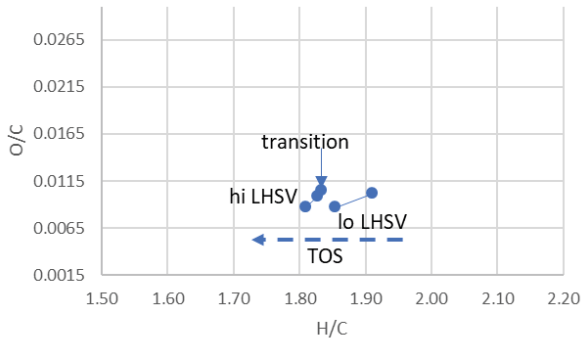


Figure 7.13. van Krevelen plot of hydrotreated products from catalytic pyrolysis

thereafter. This underscores that there was a break-in period for the catalyst but thereafter it was fairly stable.

For the purposes of this thesis, a van Krevelen analysis has been applied to the hydrotreating products. As seen in Figure 7.13, The change in product

compositions over the time of the experiment (307 h) suggest only a minor change in the catalyst activity moving toward a slightly less saturated product, but also a more deoxygenated one. Note that the low LHSV test samples were recovered earlier in the test; the point labeled transition was also recovered after low LHSV processing although it appears to be more representative of the high LHSV products, which followed chronologically. Although a visual inspection might suggest the two groups of data points based on LHSV, the alternative explanation of a group of products with only a single outlier (the lo LHSV product from the beginning of the test) might be the better assessment, as it better aligns with the SimDist data.

7.3.3. REACTION MECHANISM OF HYDROTREATMENT

The catalytic pyrolysis bio-oil performed well for up to 307 h when using a single bed catalyst configuration. The catalytic pyrolysis bio-oil has some advantages for upgrading compared to the two-stage upgrading of the non-catalytic bio-oil,[113] including higher yields of gasoline and diesel range molecules and less tendency to coke. The products from the tests were similar to those obtained from the two-stage hydrotreating of the non-catalytic bio-oil[5]. The light oil phase product was sufficiently hydrotreated so that nitrogen and sulfur were at or below the level of detection, while the residual oxygen content was low, about 1 %. The density of the products ranged from 0.79 g/mL to 0.825 g/mL over the period of the test, which correlated with a change of the hydrogen to carbon atomic ratio from 1.91 down to 1.81, suggesting little loss of catalyst activity after the initial break-in period.

The major differences observed in the hydrotreating performance of the red mud catalytic pyrolysis oils and the three and two-stage hydrotreating of the non-catalytic pyrolysis oils could be attributed to the stability of the oils. Elliott, et al.[130] Olarte, et al.[131] and de Miguel Mercader, et al.[132] showed that a mild hydrotreatment of the non-catalytic pyrolysis oils reduced the oxygen levels of the oils and produced a relatively stable oils that were processed under more severe hydrotreating conditions without causing severe coking of the hydrotreating catalyst. The coking of the hydrotreating catalysts was attributed

130 Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Zacher, A.H. Environmental Process and Sustainable Energy, 2009, 28(3), 441-449.

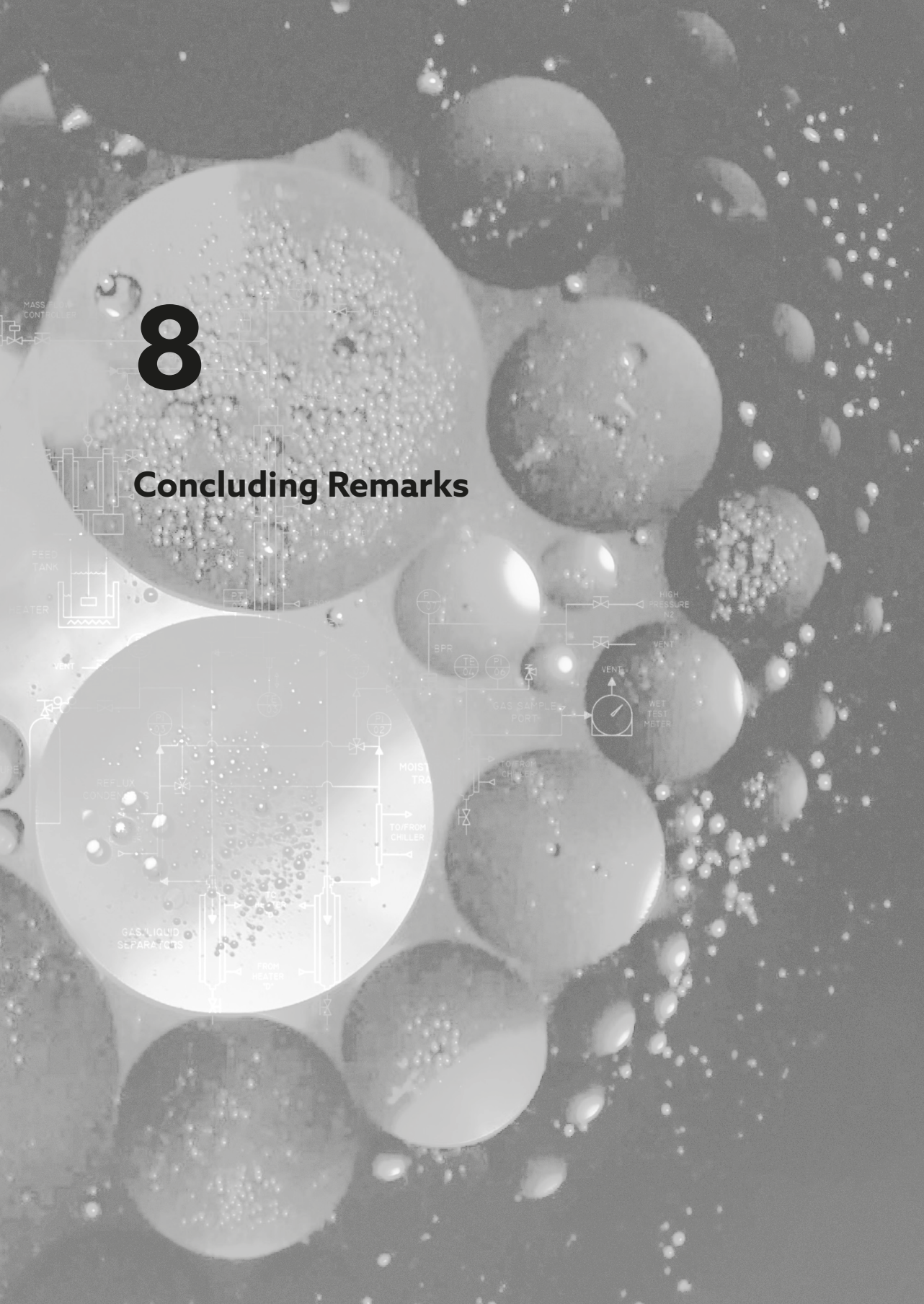
131 Olarte, M.V.;Zacher, A.H.; Padmaperuma, A.B.; Burton, S.D.; Job, H.M.; Lemmon, T.L.; Swita, M.S.; Rotness, L.J.; Neuenschwander, G.N.; Frye, J.G.; Elliot, D.C. Topics in Catalysis, 2016, 59, 55-64.

132 De Miguel Mercader, F.; Groenneveld, M.J.; Kersten, S.R.A.; Way, N.W.J.; Schaverien, C.J.; Hogendoorn, J.J. Applied Catalysis B; Environ. 2010, 96, 57-66.

to the formation of polymeric materials (humic sunstances) during the severe treatment of the bio-oil. Agblevor et al.[112] showed that catalytic pyrolysis oils produced from poplar wood were very stable and were co-processed with standard gas oil without severe coke formation. Mercader et al.[132] also showed that initial mild hydrotreating of non-catalytic pyrolysis oils made them stable to be co-processed with long residue without causing excessive coke formation. These studies suggest that the catalytic pyrolysis oils perhaps have similar properties as the mildly hydrotreated oils in terms oil stability and therefore could be processed under severe hydrotreating condition without catalysts fouling. The current results suggest that the catalytic pyrolysis oils may be more stable or equivalent to the mildly hydrotreated oils and therefore hydrotreatment in a single stage reactor was feasible. The mild hydrotreatment in the first stage in the three and two-stage processes is used to stabilize the labile reactive species in the non-catalytic pyrolysis bio-oil which form polymeric material that plug the reactor resulting in pressure build up in the reactor during severe hydrotreating process.[129] In contrast the catalytic pyrolysis using the red mud achieved a similar stabilization of the oil *in situ*. However, a detailed analysis of the mild hydrotreated bio-oil and the red mud catalytic pyrolysis will be necessary to answer the question of the equivalence of the two products.

7.4. CONCLUSIONS

- Red mud which is a waste material from the aluminum industry appears to be an effective catalyst for biomass pyrolysis for the production of low oxygenated and low viscosity oils which were relatively stable. The improved properties of the catalytic pyrolysis oils facilitated the single stage upgrading of the oils in a hydrotreater. The viscosity of the catalytic pyrolysis oil was directly correlated with the alcohol/ether carbon contents of the oils. Reducing these groups in the oils appeared to improve the viscosity and reduce aging rate of the oils.
- There was no evidence of catalyst fouling in more than 300 h time-on-stream processing of the red mud catalytic pyrolysis oils and nearly complete deoxygenation was accomplished at severe processing conditions with sulfided catalyst and high yield of hydrotreated bio-oil product was achieved.



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Concluding Remarks

The chapters of this thesis demonstrate that a range of bio-oil products can be transformed by catalytic hydrotreatment in a trickle-bed reactor to produce primarily hydrocarbon mixtures. The different bio-oil types, which were processed, can have different results relative to ease of processing due to trace component content or thermal stability related to oxygenated component types. The products can vary based on component types as well as yield structure.

A van Krevelen analysis of the various hydrotreated products is presented in Figure 8.1. The samples were derived from the data from each of the six papers discussed in this thesis. A representative sample from midrange in the experiments was chosen so as to be neither start-up activity of the catalysts nor after significant deactivation of the catalysts. The products are all much different from the feedstocks, which would be placed well off the chart to the upper left side. The different products are somewhat clustered as suggested by the three ovals placed on the chart. The bioCRACK products are high quality with low oxygen contents but very high levels of hydrogenation. It is possible that the bioCRACK products are biased by a residual petroleum contamination from the carrier used in the process. The hydrotreated catalytic pyrolysis bio-oil is also good quality, but with less hydrogenation. The phenolic oils have noteably higher oxygen contents. The hot vapor filtered products are similar to the unfiltered products, with the switchgrass products having much higher oxygen contents than the red oak products. The red oak products are similar to the pine products from conventional fluid-bed fast pyrolysis. Compared to the pine bio-oil products, the heavy phase product has somewhat less hydrogenation and the top phase (resin) product is even less saturated and with higher residual oxygen. The CoMo and NiMo products from pine bio-oil are not much different by this analysis, as they are closely clustered together.

Operation of two-stage (non-isothermal) hydrotreatment in a continuous-flow trickle-bed reactor was demonstrated at bench-scale for up to 100 h of time on stream. Plugging due to particulate was noted suggesting a need to filter bio-oil produced in fluidized bed fast pyrolysis systems. The sulfided CoMo on C catalyst had a limited lifetime. A NiMo sulfide catalyst was also active with a slightly higher level of hydrogenation noted versus the CoMo catalyst.

A phase-separated (more-dense, less-water-soluble phase) fast pyrolysis bio-oil was more easily hydrotreated, apparently due to separation of less stable components in a more-water-soluble phase. As a result of the separation of the bio-oil and use of only the heavy, less-water-soluble phase, these tests were able to continue for a much longer period of time on stream (246 h)

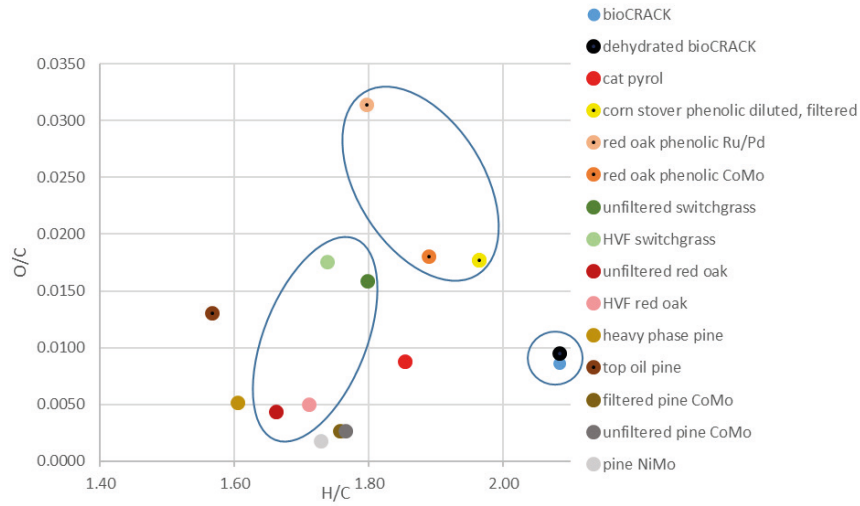

Figure 8.1. Van Krevelen analysis of the various hydrotreated bio-oil products

without fouling of the bed. The operating temperatures of the two beds were in the range of 270 °C and 445 °C (due to significant exothermic reaction in the higher temperature bed). Highly deoxygenated products were produced which could be readily fractionated by distillation. The O content of the hydrotreated product was 0.6 wt % with most of the O found in the vacuum distillate range (up to 380 °C). The distillate residue amounted to only 5.5 wt % of the product Analysis of the distillate fractions showed a preponderance of cyclic hydrocarbons, both aromatic and aliphatic. A low yield of a vacuum distillation residue was recovered with potential for production of a coke for electrothermic metal (such as Al) refining.

Hydrotreatment of hot-vapor filtered bio-oil products was compared to hydrotreatment of non-filtered bio-oils from the same feedstocks (red oak and switchgrass). The effects through 60 h tests in a two-stage hydrotreater system were minimal. The products from the four tests were similar, but the red oak products were notedly different from the switchgrass products, having less residual oxygen. The high-quality products were produced with little evidence of catalyst deactivation. The light oil phase product was fully hydrotreated so that nitrogen and sulfur were below the level of detection, while the residual oxygen ranged from 0.3 to 2.0 %. The density of the products varied from 0.80 g/mL up to 0.86 g/mL over the period of the test with a correlated change of the hydrogen to carbon atomic ratio from 1.79 down to 1.57, suggesting

some loss of catalyst activity through the test. The differences in the results were minimized because the non-filtered bio-oils were very low in inorganic contamination, as produced in the entrained-flow pyrolysis unit equipped with a bio-oil filtration step. The slightly higher amount of mineral deposition on the catalysts from the switchgrass test was noted but appeared to have little effect on the process. These tests provided the data needed to assess the suite of liquid fuel products from the process and the activity of the catalyst in relationship to the existing catalyst lifetime barrier for the technology.

A primarily phenolic fraction of bio-oil was hydrotreated following its fractionation and recovery in fluid-bed pyrolysis pilot plant. Phenolic fractions from red oak and corn stover were compared. The phenolic fractions were found to contain lower levels of inorganic contamination compared to whole bio-oil. The chemical composition was clearly biased toward phenolic with reduced carbonyl, carboxyl and other light oxygenates. Several precious and base metal catalysts were tested. The precious metal catalysts (Pd/Re, Ru and Pd) produced more hydrogenated products with higher H/C ratios but with higher residual oxygen contents. There was substantial heteroatom removal with residual O of only 0.4 % to 5 %, while N and S were reduced to less than 0.05 % (the level of detection). Use of the precious metal catalysts resulted in more saturated products, but less completely hydrotreated compared to the sulfided CoMo metal catalyst, which was operated at higher temperature and lower space velocity. The sulfided CoMo catalyst produced a more deoxygenated product with lower density. The liquid product was 42-52 % gasoline range molecules and about 43 % diesel range molecules.

Corn stover-derived phenolic oils were more difficult to process because of higher particulate levels. Blockage by particulate was a major issue, showing that filtration of the feed oil will be needed. This difficulty contrasts with the catalyst bed fouling and plugging, which is typically seen with hydrotreatment of whole bio-oil. In this case, the problem was substantially alleviated by filtering the phenolic oils before hydrotreating. More thorough washing of the phenolic oils during their preparation from the heavy ends of bio-oil or on-line filtration of pyrolysis vapors to remove particulate matter before condensation of the bio-oil fractions is recommended. Filtration and subsequent hydrotreating could only be accomplished following solvent dilution of the oil with isopropanol. Analysis of the spent catalysts led to the conclusion that Ru may be susceptible in the long term to S poisoning, even from the low levels of S found in these phenolic oils, while Pd may be more resistive.

The bio-oils produced by the bioCRACK pyrolysis process were also readily hydrotreated to hydrocarbons with removal of oxygen to low levels. Only a single stage hydrotreater was used in these tests showing that the lower temperature stabilization step was not needed in contrast to its requirement for processing conventional fast pyrolysis bio-oils. Tests performed at 400 °C with a sulfided CoMo catalyst showed stable operation over 54 and 62 h without bed plugging or loss of catalyst activity. The condensed liquid products were analyzed and found that the hydrocarbon liquid was significantly hydrotreated so that nitrogen and sulfur were below the level of detection (<0.05), while the residual oxygen ranged from 0.7 to 1.2 %. The density of the products varied from 0.71 g/mL up to 0.79 g/mL with a correlated change of the hydrogen to carbon atomic ratio from 2.1 down to 1.9. The product quality remained high throughout the extended tests suggesting minimal loss of catalyst activity through the test. The relatively clean bioCRACK feedstock oils left only slightly measurable mineral deposits in the catalyst beds.

Similarly, catalytic pyrolysis bio-oils were processed through a single-stage hydrotreating bed to produce high quality products without a preliminary low-temperature stabilization step. Low viscosity bio-oils produced from pinyon juniper using a red mud catalyst, *in situ*, in the fluid-bed pyrolysis system were recovered in lower yield than uncatalyzed fast pyrolysis but with sufficiently modified character that their thermal stability was not an issue in the catalytic hydrotreater operated at 400 °C. Hydrocarbon fuel products with density of 0.80-0.82 g/mL and low oxygen content were formed. There was no evidence of catalyst fouling in a >300 h test which produced a nearly deoxygenated product at high yield.

Using data from the six articles, it is possible to make calculations of the overall carbon efficiencies of the several process configurations. Data is presented in Table 8.1 using selected products as were used in the van Krevelen analysis above. From this table it is possible to make comparisons of the several process configurations. Using the pine data as the baseline, 20 to 25 percent of the carbon in the biomass is recovered in the hydrocarbon liquid product. Even though the top oil phase and the phase-separated heavy phase are converted to hydrocarbon at higher efficiencies by the hydrotreating step, the lower yield from the pyrolysis leads to an overall lower yield. However, the top phase, which can be recovered in some cases from softwood fast pyrolysis, clearly is a useful feedstock for hydrotreating to liquid fuels. The loses to the lighter, more aqueous phase in phase-separated bio-oil cleanly reduce the overall yield

Table 8.1 Carbon efficiency calculations for pyrolysis and hydrotreating

Sample	% C in biomass	% yield of bio-oil	% C in bio-oil	% C yield bio-oil	% oil yield HT	% C, HT bio-oil	%C yield HT	%C yield overall
pine bio-oil CoMo	49.5%	62.5%	53.0%	66.9%	37.0%	84.6%	31.3%	20.9%
pine bio-oil NiMo	49.5%	62.5%	53.0%	66.9%	38.0%	84.6%	32.1%	21.5%
top oil pine	49.5%	1.0%	55.1%	1.1%	42.0%	86.5%	36.3%	0.4%
heavy phase bio-oil	49.5%	22.0%	54.5%	24.2%	56.7%	87.4%	49.6%	12.0%
unfiltered switchgrass	43.2%	56.3%	43.3%	56.4%	43.0%	85.3%	36.7%	20.7%
HVF switchgrass	43.2%	52.3%	38.1%	46.1%	46.0%	85.5%	39.3%	18.1%
unfiltered red oak	49.6%	68.1%	42.2%	57.9%	48.0%	87.3%	41.9%	24.3%
HVF red oak	49.6%	63.5%	37.3%	47.8%	40.0%	86.9%	34.8%	16.6%
corn stover phenolic	43.2%	9.0%	74.4%	15.6%	58.0%	83.0%	48.2%	7.5%
red oak phenolic Ru/Pd	49.6%	10.7%	65.6%	14.2%	59.9%	82.1%	49.2%	7.0%
red oak phenolic CoMo	49.6%	10.7%	65.6%	14.2%	61.4%	82.3%	50.5%	7.2%
bioCRACK	50.7%	21.0%	51.1%	21.2%	30.0%	84.3%	25.3%	5.3%
dehydrated bioCRACK	50.7%	4.2%	59.1%	4.9%	53.0%	85.5%	45.3%	1.9%
catalytic pyrol	49.5%	30.0%	70.2%	42.6%	75.0%	85.7%	64.3%	27.4%

of liquid hydrocarbons, meaning that a large portion of the hydrotreatable pyrolysis product is contained in the aqueous phase. The unfiltered red oak and switchgrass bio-oils result in similar liquid hydrocarbon yields as the pine. However, the loses in the hot vapor filtration step lead to significant reductions in hydrocarbon liquids. The phenolic oils recovered from fractionated bio-oils are also useful hydrotreating feedstocks, but their much smaller yields result in greatly reduced yields of liquid hydrocarbon. Of course, the balance of the pyrolysis product is envisioned as chemical feedstock through other processing steps. The bioCRACK process provides an alternative pyrolysis pathway for liquefying biomass; however, the very low yields of the liquid products result in very low overall yields of liquid hydrocarbon, even considering that overall yield is the sum of the two products. Finally, catalytic pyrolysis results in the most promising carbon efficiency, in the range of 25 to 30 % overall. Its lower pyrolysis yield is more than compensated by the higher yield in the hydrotreating step. The data was generated through the use of a non-acidic solid oxide catalyst in the pyrolysis step, which has been shown to have potential for regeneration and a much longer life than the typical solid acidic catalysts.

Altogether these results suggest that optimum bio-oil compositions for hydrotreating to hydrocarbon fuels may not be the same as optimum compositions from highest yielding fast pyrolysis processes. Improved operability in hydrotreating can be achieved by fractionation of the bio-oil through phase separation, fractional collection, hot vapor filtration, or the bioCRACK process. Removal of light oxygenates, such as sugars, acids and aldehydes appears to be the key change with these process modifications. On the one hand, these materials are only likely to produce hydrocarbon liquid fuels if they undergo condensation reactions and their removal is not likely to reduce liquid product yields on an equimolar basis; unfortunately, other potentially hydrotreatable components are also lost, such that the overall yields are reduced. Of greater interest is catalytic pyrolysis, which can result in bio-oil products that are more amenable to hydrotreating, due to changes in composition, and it results in an overall greater yield of hydrocarbon liquids through a simplified treatment involving only one stage of hydroprocessing.

9. SUMMARY

One pathway from renewable biomass feedstocks to replacements for liquid fuels from fossil sources is the fast pyrolysis pathway. Catalytic hydroprocessing of fast pyrolysis bio-oil is intended to improve the fuel quality from the highly oxygenated products from fast pyrolysis to a hydrocarbon mixture, which could serve as a fuel in conventional transportation systems. Catalytic hydroprocessing of bio-oil has been under development for nearly 40 years. This thesis includes studies to further advance the state of technology of bio-oil hydrotreating by describing experimental work of an applied nature with a strong under-pinning of chemical mechanistic understanding, catalytic material analysis, and fuel property considerations. The chapters describe some of the most recent efforts in converting several types of biomass fast pyrolysis bio-oils to hydrocarbon mixtures with potential use as fuel blending components. These chapters describe bench-scale experiments in the hydroprocessing of a range bio-oil products including conventional fluid-bed pyrolysis products, hot-vapor filtered bio-oil from an entrained flow reactor, fractionated bio-oil from a conventional fluid-bed reactor as well as from an experimental system using recycled oil in the fluid-bed reactor, and finally a catalytic pyrolysis product, which is an *in situ* stabilized (deoxygenated) fast pyrolysis bio-oil product. The tests were undertaken in continuous-flow tubular fixed-bed reactors configured for trickle-bed operation with hydrogen and bio-oil both fed cold, co-currently into the top of the preheated reactor.

Operation of two-stage (non-isothermal) hydrotreatment in a continuous-flow trickle-bed reactor was demonstrated at bench-scale for up to 100 h of time on stream. Plugging due to particulate was noted suggesting a need to filter bio-oil produced in fluidized bed fast pyrolysis systems. The sulfided CoMo on C catalyst had a limited lifetime. A NiMo sulfide catalyst was also active with a slightly higher level of hydrogenation noted versus the CoMo catalyst.

A phase-separated (more-dense, less-water-soluble phase) fast pyrolysis bio-oil was more easily hydrotreated, apparently due to separation of less stable components in a more-water-soluble phase. As a result of the separation of the bio-oil and use of only the heavy, less water-soluble phase, these tests were able to continue for a much longer period of time on stream (246 h) without fouling of the bed. The operating temperatures of the two beds were in the range of 270 °C and 445 °C (due to significant exothermic reaction in the higher temperature bed). Highly deoxygenated products were produced which could be

readily fractionated by distillation. The O content of the hydrotreated product was 0.6 wt % with most of the O found in the vacuum distillate range (up to 380 °C). The distillate residue amounted to only 5.5 wt % of the product. Analysis of the distillate fractions showed a preponderance of cyclic hydrocarbons, both aromatic and aliphatic. A low yield of a vacuum distillation residue was recovered with potential for production of a coke for electrothermic metal (such as Al) refining.

Hydrotreatment of hot-vapor filtered bio-oil products was compared to hydrotreatment of non-filtered bio-oils from the same feedstocks (red oak and switchgrass). The effects through 60 h tests in a two-stage hydrotreater system were minimal. The products from the four tests were similar, but the red oak products were notedly different from the switchgrass products, by having less residual oxygen. The high-quality products were produced with little evidence of catalyst deactivation. The light oil phase product was fully hydrotreated so that nitrogen and sulfur were below the level of detection, while the residual oxygen ranged from 0.3 to 2.0 %. The density of the products varied from 0.80 g/mL up to 0.86 g/mL over the period of the test with a correlated change of the hydrogen to carbon atomic ratio from 1.79 down to 1.57, suggesting some loss of catalyst activity through the test. The differences in the results were minimized because the non-filtered bio-oils were very low in inorganic contamination, as produced in the entrained-flow pyrolysis unit equipped with a bio-oil filtration step. The slightly higher amount of mineral deposition on the catalysts from the switchgrass test was noted but appeared to have little effect on the process. These tests provided the data needed to assess the suite of liquid fuel products from the process and the activity of the catalyst in relationship to the existing catalyst lifetime barrier for the technology.

A primarily phenolic fraction of bio-oil was hydrotreated following its fractionation and recovery in fluid-bed pyrolysis pilot plant. Phenolic fractions from red oak and corn stover were compared. The phenolic fractions were found to contain lower levels of inorganic contamination compared to whole bio-oil. The chemical composition was clearly biased toward phenolic with reduced carbonyl, carboxyl and other light oxygenates. Several precious and base metal catalysts were tested. The precious metal catalysts (Pd/Re, Ru and Pd) produced more hydrogenated products with higher H/C ratios but with higher residual oxygen contents. There was substantial heteroatom removal with residual O of only 0.4 % to 5 %, while N and S were reduced to less than 0.05 % (the level of detection). Use of the precious metal catalysts resulted in more saturated

products, but less completely hydrotreated compared to the sulfided CoMo metal catalyst, which was operated at higher temperature and lower space velocity. The sulfided CoMo catalyst produced a more deoxygenated product with lower density. The liquid product was 42-52 % gasoline range molecules and about 43 % diesel range molecules.

Corn stover-derived phenolic oils were more difficult to process because of higher particulate levels. Blockage by particulate was a major issue, showing that filtration of the feed oil will be needed. This difficulty contrasts with the catalyst bed fouling and plugging, which is typically seen with hydrotreatment of whole bio-oil. In this case, the problem was substantially alleviated by filtering the phenolic oils before hydrotreating. More thorough washing of the phenolic oils during their preparation from the heavy ends of bio-oil or on-line filtration of pyrolysis vapors to remove particulate matter before condensation of the bio-oil fractions is recommended. Filtration and subsequent hydrotreating could only be accomplished following solvent dilution of the oil with isopropanol. Analysis of the spent catalysts led to the conclusion that Ru may be susceptible in the long term to S poisoning, even from the low levels of S found in these phenolic oils, while Pd may be more resistive.

The bio-oils produced by the bioCRACK pyrolysis process were also readily hydrotreated to hydrocarbons with removal of oxygen to low levels. Only a single stage hydrotreater was used in these tests showing that the lower temperature stabilization step was not needed in contrast to its requirement for processing conventional fast pyrolysis bio-oils. Tests performed at 400 °C with a sulfided CoMo catalyst showed stable operation over 54 and 62 h without bed plugging or loss of catalyst activity. The condensed liquid products were analyzed and found that the hydrocarbon liquid was significantly hydrotreated so that nitrogen and sulfur were below the level of detection (<0.05), while the residual oxygen ranged from 0.7 to 1.2 %. The density of the products varied from 0.71 g/mL up to 0.79 g/mL with a correlated change of the hydrogen to carbon atomic ratio from 2.1 down to 1.9. The product quality remained high throughout the extended tests suggesting minimal loss of catalyst activity through the test. The relatively clean bioCRACK feedstock oils left only slightly measurable mineral deposits in the catalyst beds.

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recovered in lower yield than uncatalyzed fast pyrolysis but with sufficiently modified character that their thermal stability was not an issue in the catalytic hydrotreater operated at 400 °C. Hydrocarbon fuel products with density of 0.80-0.82 g/mL and low oxygen content were formed. There was no evidence of catalyst fouling in a >300 h test which produced a nearly deoxygenated product at high yield.

The chapters of this thesis demonstrate that a range of bio-oil products can be transformed by catalytic hydrotreatment in a trickle-bed reactor to produce primarily hydrocarbon mixtures. The different bio-oil types, which were processed, can have different results relative to ease of processing due to trace component content or thermal stability related to oxygenated component types. The products can vary based on component types as well as yield structure.

10. SAMENVATTING

Pyrolyse is een interessante route om vaste biomassa om te zetten in vloeibare producten. Echter de producteigenschappen van de gevormde pyrolyse oliën zijn zodanig dat deze niet direct toepasbaar zijn als transportbrandstof. Een mogelijke technologie om de producteigenschappen te verbeteren is een katalytische waterstof behandeling. Tijdens deze behandeling worden de zuurstof bevattende componenten omgezet in een mengsel van koolwaterstoffen. Dit proefschrift beschrijft onderzoek naar de omzetting van pyrolyse oliën naar transportbrandstoffen met behulp van deze katalytische waterstof behandeling. Het onderzoek was experimenteel van aard en had als doelstellingen om meer inzicht te krijgen in i) het effect van de samenstelling van de voeding op het proces en de product eigenschappen, ii) relevante moleculaire omzettingen, iii) de rol van de katalysator en met name mogelijke deactiverings routes en iv) het bepalen van proces-product relaties. De experimenten werden uitgevoerd met een aantal verschillende pyrolyse olie voedingen in continue geopereerde vaste bed reactoren in het zogenaamde trickle flow regiem. De gebruikte laboratorium schaal reactoren werden typisch geopereerd met twee verschillende temperatuur niveaus.

Testen met een conventionele pyrolyse olie en gesulfideerde CoMo en NiMo katalysatoren gaven "plugging" van de reactor als gevolg van deeltjesvorming bij runtijden > 100 h, hetgeen suggereert dat het nodig is om de pyrolyse olie te filtreren voor gebruik. Voor met name de gesulfideerde CoMo katalysator op een kool drager was de stabiliteit gelimiteerd. De gesulfideerde NiMo katalysator liet een enigszins hogere hydrogenerings activiteit zien dan de CoMo-katalysator.

In een vervolgstap werd de water onoplosbare fase van een fase-gescheiden pyrolyse olie gebruikt en deze olie was beter te behandelen dan de originele pyrolyse olie. Het bleek mogelijk om de reactor gedurende 246 h te opereren zonder operationele problemen bij bed temperaturen tussen 270 °C en 445 °C. Dit duidt erop dat de water onoplosbare fase minder instabiele componenten bevat dan de waterfase. Een sterk gedeoxygeneerde olie werd gevormd (0.6 gew% O), die gemakkelijk konden worden gefractioneerd door middel van destillatie. Analyse van de destillatie fracties liet een grote hoeveelheid aan cyclische koolwaterstoffen zien, zowel aromatische als alifatische. Het destillatie residu was verassend laag (5.5 gew.%). Dit product kan mogelijk omgezet worden in een coke met mogelijke toepassingen in de staal en aluminiumindustrie.

Daarnaast werd onderzoek gedaan naar de katalytische waterstof behandeling van hete damp gefiltreerde pyrolyse oliën en de resultaten werden vergeleken met resultaten van de niet-gefilterde pyrolyse oliën uit dezelfde grondstoffen (rode eik en switchgras). Vergelijkbare resultaten werden verkregen voor de reacties met gefilterde en ongefilterde oliën gedurende runtijden van 60 uur. De samenstelling van de product oliën van beide voedingen was echter behoorlijk verschillend. Zo was het zuurstofgehalte van de oliën gemaakt van rode eik beduidend lager dan die gemaakt van switchgras. Het stikstof en zwavelgehalte van de producten lag onder het detectieniveau, het zuurstofgehalte varieerde van 0.3 tot 2.0 %. De dichtheid van de producten varieerde van 0.80 tot 0.86 g/ml gedurende de test, de H/C verhouding tussen 1.79 en 1.57, hetgeen enig verlies van katalysator activiteit tijdens de testen suggereert.

In een vervolgstap werd een fenolische fractie van een aantal pyrolyse oliën (uit rode eik en mais residuen) gebruikt voor een katalytische waterstof behandeling. Analyse van de fenolische fracties liet zien dat de hoeveelheid aan zouten lager is dan die in de oorspronkelijke pyrolyse oliën. Verschillende typen metaal katalysatoren werden getest. De edelmetaal katalysatoren (Pd/Re, Ru en Pd) gaven producten met hogere H/C-verhoudingen dan CoMo maar met hogere zuurstofgehaltes. Vluchtigheid analyses van de product oliën gaven aan dat ongeveer 42-52 % van de producten in de benzine range en ongeveer 43 % in de diesel range lagen.

De van mais residuen afgeleide fenolische oliën waren moeilijker te verwerken vanwege hogere gehaltes aan vaste deeltje. Dit leidde tot verstopping van de katalysator bedden. Dit probleem kon worden opgelost door de fenolische oliën te filtreren voorafgaand aan de reactie. Filtratie en daaropvolgende katalytische waterstof behandeling konden alleen worden uitgevoerd na verdunning van de olie met isopropanol. Analyse van de gebruikte katalysatoren leidde tot de conclusie dat de aanwezigheid van zwavel in de voeding kan leiden katalysator deactivering, met name bij gebruik van Ru.

De pyrolyse oliën geproduceerd met een bioCRACK pyrolyseproces bleken ook prima om te zetten tot producten met lage zuurstofgehaltes. In dit geval werd de reactor geopereerd bij 1 in plaats van 2 temperatuur niveaus. Klaarblijkelijk is een lage temperatuur stabilisatiestap niet nodig voor deze oliën, in tegenstelling tot conventionele pyrolyse oliën. Experimenten bij 400 °C met

een gesulfideerde CoMo-katalysator vertoonden stabiele operatie gedurende 54-62 uur zonder verstopping van het bed of verlies van katalysator activiteit. De vloeibare producten werden geanalyseerd. Stikstof en zwavel niveaus lagen onder de detectie limiet (< 0.05 gew%), terwijl het zuurstofgehalte varieerde van 0.7 tot 1.2 gew%. De dichtheid van de producten varieerde van 0.71 tot 0.79 g/ml, met een gecorreleerde verandering van de H/C ratio van 2.1 tot 1.9. Bij gebruik van de relatief schone bioCRACK-pyrolyse oliën was de minerale afzetting in de katalysatorbedden minimaal.

Als laatste werden pyrolyse oliën uit een katalytisch pyrolyseproces gebruikt voor een enkeltraps katalytische waterstof behandeling om producten van hoge kwaliteit te produceren zonder een voorafgaande stabilisatiestap bij lage temperatuur. Hierbij werd een zogenaamde red-mud katalysator gebruikt. Producten met een dichtheid van 0.80-0.82 g/ml en een laag zuurstofgehalte werden verkregen. Er was geen bewijs voor katalysator deactivering in een > 300 uur test.

De research beschreven in dit proefschrift toont aan dat een breed scala aan pyrolyse oliën kunnen worden omgezet in koolwaterstof rijke producten met een laag zuurstofgehalte middels een katalytische waterstof behandeling in een trickle bed reactor. De verwerkbaarheid van de verschillende pyrolyse oliën is afhankelijk van het gehalte aan sporenelementen en de thermische stabiliteit van de voeding, die gerelateerd is aan de aanwezigheid van bepaalde geoxygeneerde componenten. De opbrengst en de samenstelling van de product oliën blijkt sterk afhankelijk te zijn van de gebruikte voedingen.

11. ACKNOWLEDGEMENTS

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The author is also grateful to his colleagues at PNNL (many named as authors on the papers included here) who over the years supported and contributed to the progress of the bio-oil hydrotreating research field through feedstock preparation, reactor operation and maintenance, and the chemical and physical analysis of the feedstocks and products. In particular, Eddie G. Baker, who is not listed on these later publications, contributed mightily in the early years and is a named author on many the fundamental research papers in the field.

In addition to the coauthors listed in the papers included here, there are many other contributing staff at PNNL, as well as the research partner institutes, the Technical Research Centre of Finland, Iowa State University, the National Renewable Energy Laboratory, BDI-Bioenergy, and Utah State University, which I acknowledge for their roles in the research. The descriptions of the bio-oil production at the partner facilities were authored by them, while the descriptions of the hydrotreating work at PNNL was authored by the PNNL contributors.

I also acknowledge the contribution from Dr. R.H. Venderbosch in encouraging me to push the data a bit further in this final thesis form, in particular the van Krevelen and carbon efficiency analyses, to get more out the earlier reported results.

Finally, I dedicate this work to my family, to my grandsons who may someday be “scientists”, to my sons, and to my wife who held our family together over the entire length of my career.

12. PUBLICATIONS

12.1. INCLUDED IN THIS THESIS

Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Olarte, M.V.; Zacher, A.H.; Solantausta, Y. 2012. "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust." **Energy & Fuel** *26,* 3891-3896. web published May 29, 2012.

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12.2. RECENT REVIEW ARTICLES BY THE AUTHOR

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