

Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover

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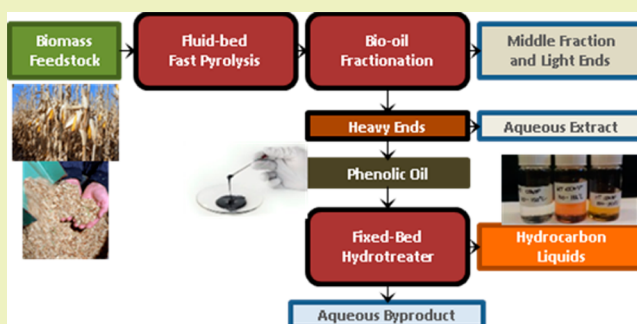
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ABSTRACT: Phenolic oils were produced from fast pyrolysis of two different biomass feedstocks, red oak and corn stover, and evaluated in hydroprocessing tests for production of liquid hydrocarbon products. The phenolic oils were produced with a bio-oil 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 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. They were effective in removing heteroatoms with carbon yields as high as 81% (unadjusted for the 90% carbon balance). 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%. Use of the precious metal catalysts resulted in more saturated products less completely hydrotreated compared to the sulfided base metal catalyst, which was operated at higher temperature. The liquid product was 42–52% gasoline range molecules and about 43% diesel range molecules. Particulate matter in the phenolic oils complicated operation of the reactors, causing plugging in the fixed-beds especially for the corn stover phenolic oil. This difficulty contrasts with the catalyst bed fouling and plugging, which is typically seen with hydrotreatment of whole bio-oil. This 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 online filtration of pyrolysis vapors to remove particulate matter before condensation of the bio-oil fractions is recommended.

KEYWORDS: Biomass, Pyrolysis, Fractionation, Hydrotreating, Catalysis, Fuels



INTRODUCTION

Fast pyrolysis of biomass is widely held to be a viable technology for the direct production of liquid fuels.¹ 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 hydro-treatment and catalytic cracking.² Hence, catalytic hydro-processing has been developed to convert the highly oxygenated bio-oil components into hydrocarbon liquids.³ Much of the recent work in bio-oil hydrotreating has been performed using precious metal catalysts⁴ in small batch reactors for short periods of time.⁵ In contrast, the work reported here is performed in continuous-flow reactor configuration with a presulfided catalyst that is resistant to sulfur poisoning and has been operated for days and weeks on stream.⁶

Lindfors et al.² 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.^{2,3} Sugar-type compounds are known to be susceptible to coking, and the removal of this fraction prior to upgrading protocols would be advantageous.² 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.⁷ Effective bio-oil fractionation prior to upgrading may be a valuable approach of producing liquid fuels and chemicals versus upgrading whole bio-oil.^{2,8}

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

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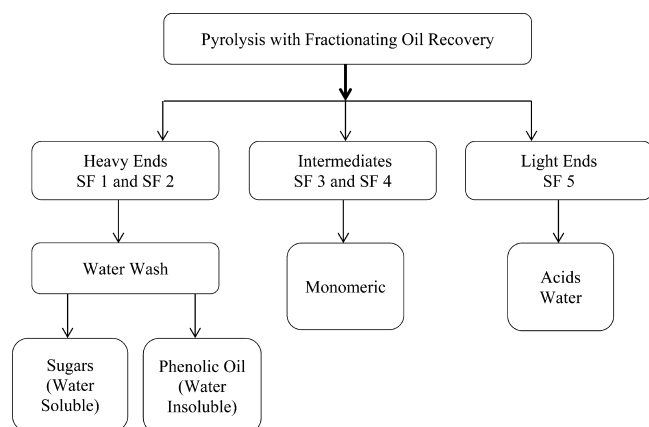


Figure 1. Procedure for the recovery of phenolic compounds from Iowa State University's bio-oil fractionating recovery system.^{3,4}

SF 4), consisting of monomeric compounds, and light ends (SF 5) that contain the majority of acids and water (Figure 1).^{9,10} Complete details on the reactor and recovery system can be found in Pollard et al.⁹ and Rover et al.¹⁰ 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.

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^{11,12} or vapor phase treatment, such as catalytic pyrolysis.¹³ 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^{3,4} on the hydrotreating process to produce liquid transportation fuels at PNNL.¹⁴

EXPERIMENTAL SECTION

Feedstocks. Predried red oak (*Quercus rubra*) chips were obtained from Wood Residual Solutions, LLC of Montecello, WI with a moisture content of approximately 10%. Cornstover feedstock (composed of leaves, stalks, and cobs) was obtained locally through ISU's Agricultural and Biosystems Engineering Department and was harvested using traditional multipass 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 3 mm 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.

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 2). Stage 1, a condenser, collects

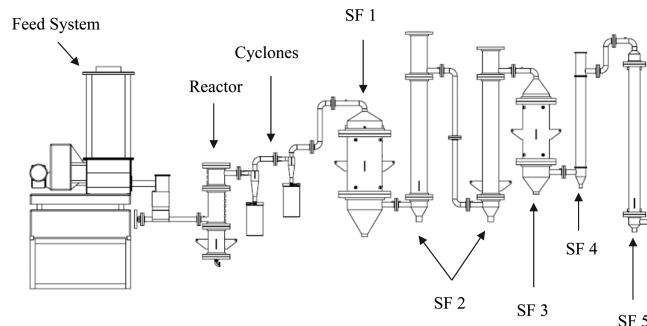


Figure 2. Process diagram for fluidized-bed reactor with fractionating condensation system.

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 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 1).^{3,4} 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 rotary evaporated at 40 °C to remove the water. Complete details can be found in Rover et al.¹⁵

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 3). In fact, the precious metal (nonsulfided) tests were performed in a different, but similar, reactor system than were the sulfided CoMo tests. In all cases the

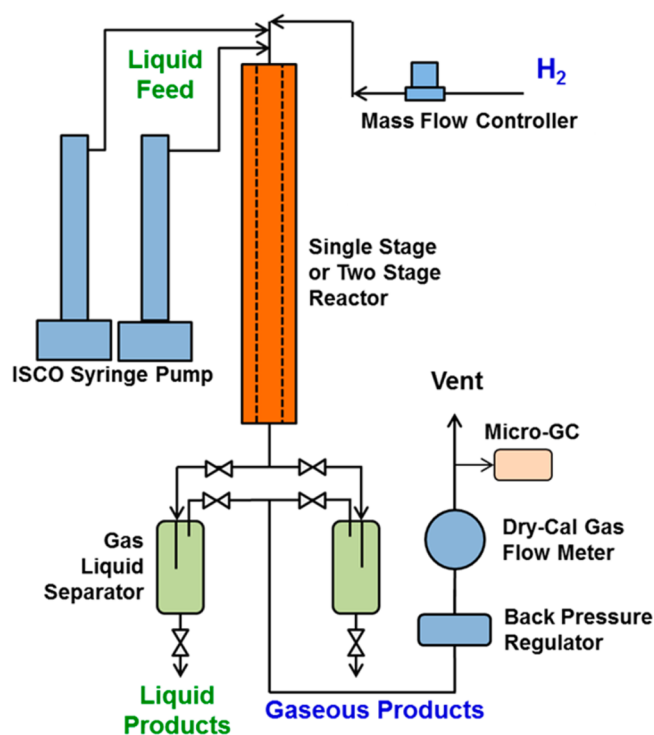


Figure 3. Schematic of the minireactor hydrotreater system.

hydrotreater was configured as a single pass, cocurrent, 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.¹⁶

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 nonsulfided catalysts as shown in Table 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, 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 H₂ flow, heated from 150 to 350 °C over 3 h in flow of H₂ and sulfiding agent (35% di-*tert*-butyl-disulfide (DTBDS) in decane), and then heated to 400 °C and held for 5 h with H₂ and sulfiding agent flowing.

For the hydroprocessing tests, the flow ratio of H₂/liquid was 2500 L H₂ (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 of S. Figure 4 shows a schematic of the catalyst beds with a superimposed 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.

Analytical Methods. Moisture content of the heavy ends from SF 1 and SF 2 were determined by titration using Karl Fisher described in literature.¹⁷ 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.³ The ultimate analysis of the phenolic oil and feedstocks were determined 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. Semiquantitative analysis of the two phenolic oils was performed with gas 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.

RESULTS

Feedstocks. Results from the analyses of the feedstocks as fed to the fast pyrolysis system are shown in Table 2. The main difference between the feedstocks is the ash, which was 20 times higher in corn stover than in oak.

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 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 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.¹⁵ 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.

Table 1. Summary of Hydrotreater Tests with Red Oak Phenolic Oil

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

^aPNNL fabricated on granular carbon, 30–60 mesh. ^bAlfa Aesar #40435, 3.5% CoO, 14%MoO₃ on alumina, ground to 30–60 mesh.

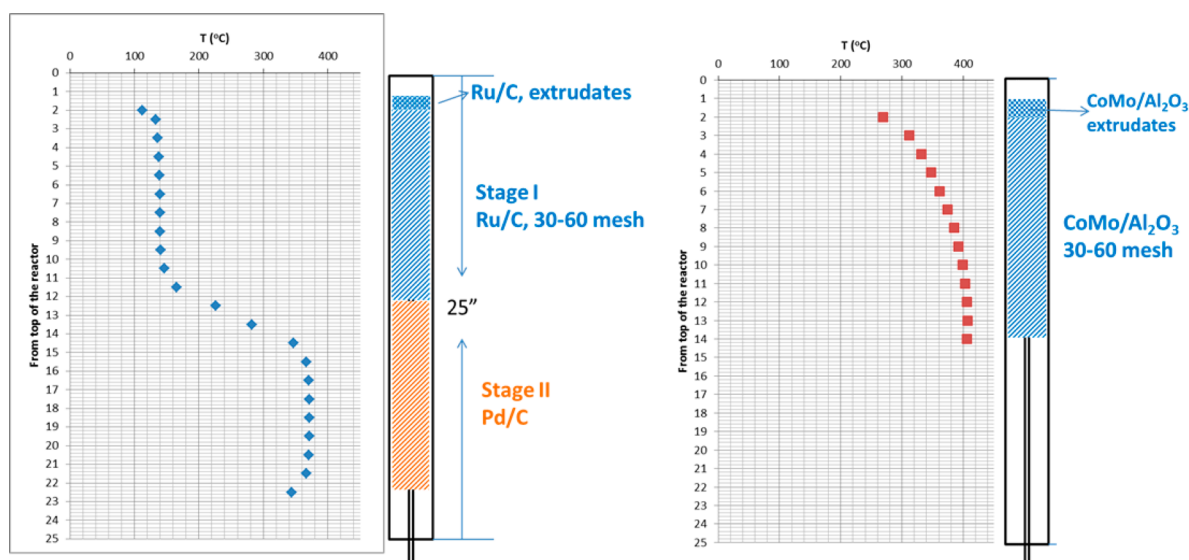


Figure 4. Schematic of the catalyst beds in the mini-hydrotreater reactor.

Table 2. Composition of Biomass Feedstocks

sample	proximate analysis, wt %				ultimate analysis, wt %				
	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

Table 3. Yields of Bio-oil Stage Fractions, Noncondensable Gases, and Char as wt % of Biomass Feed

red oak pyrolysis products		% yield (wb)	moisture %
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
noncondensable 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 (wb)	moisture %
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
noncondensable 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

Table 4. Yields of Major Gas Components as wt % of Biomass Feed

feedstock	H ₂ , wt %	CH ₄ , wt %	CO, wt %	CO ₂ , wt %	C ₂ H 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

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.

The mass yields of the major gas components are given in Table 4.

Analysis of Phenolic Oil. Table 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 and phenolic oil left moisture in the phenolic oil.

Table 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

Table 6. Components in Phenolic Oils Based on GC–MS Analysis with Relative Quantities Determined by Total Ion Current

component	retention time	phenolic oil red oak relative quantity	phenolic oil corn stover 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.

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 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 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 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 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 7, the

Table 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

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 nonphenolic 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.

Hydroprocessing Results. In the first experiment (see Table 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.¹⁸ 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 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 °C¹⁹ 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.²⁰ 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.

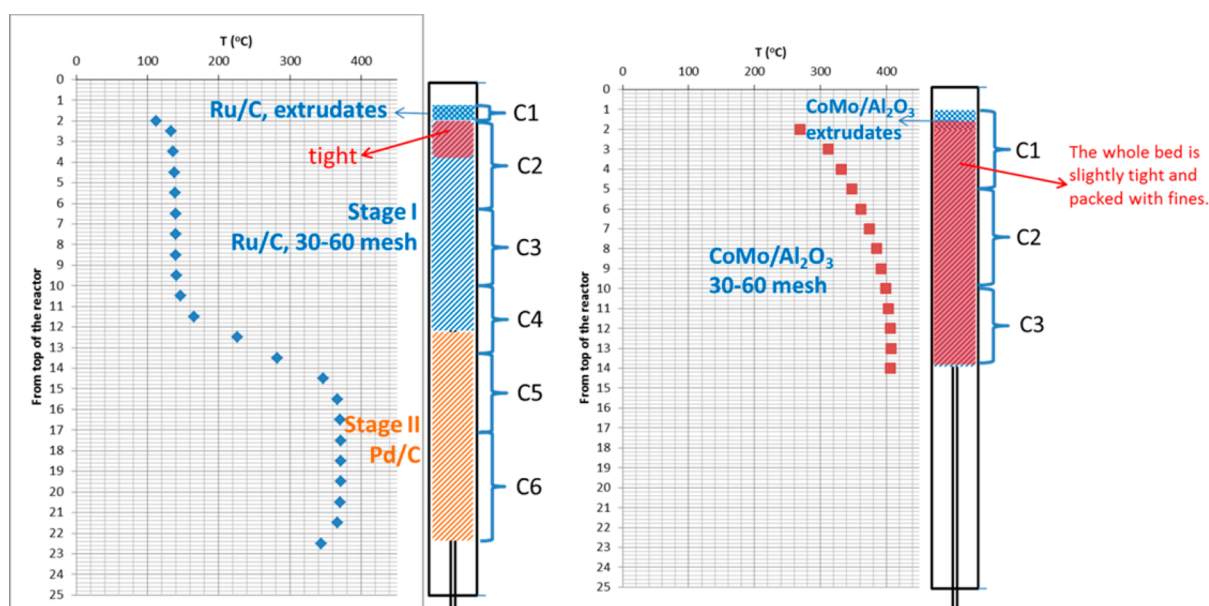


Figure 5. Schematic of the catalyst beds after use with red oak phenolic oil.

Table 8. Results from Hydroprocessing Red Oak Phenolic Oil with Ru–Pd Catalysts

TOS, h	mass yield, oil product, g dry/g dry feed	carbon yield, oil product, g C/g C in feed	oil product density, g/mL	gas yield, g per g dry feed	produced water yield, g per g dry feed	H ₂ consumed, g H ₂ /g dry feed	mass balance, %	carbon balance, %
12–18 ^a	0.585	0.719	0.87	0.074	0.164	0.042	86.9	80.5
24–30 ^b	0.599	0.748	0.85	0.104	0.217	0.037	94.6	84.8
36–42 ^b	0.657	0.812	0.88	0.083	0.189	0.039	95.2	90.4

^aHigh LHSV 0.2 in each bed (0.1 total). ^bLow LHSV 0.1 in each bed (0.05 total).

Table 9. Results from Hydroprocessing Red Oak Phenolic Oil with CoMoS Catalyst

TOS, h	mass yield, oil product, g dry/g dry feed	carbon yield, oil product, g C/g C in feed	oil product density, g/mL	gas yield, g per g dry feed	produced water yield, g per g dry feed	H ₂ consumed, g H ₂ /g dry feed	mass balance, %	carbon balance, %
4–5 ^a	0.617	0.805	0.835	0.099	0.247	0.046	93.7	90.1
12–18 ^b	0.614	0.792	0.835	0.113	0.307	0.074	96.8	92.1

^aHigh LHSV 0.5. ^bLow LHSV 0.2. For comparative data for whole bio-oil from pine, see reference 8.

Table 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 high LHSV 12–18 h	81.12	12.11	5.11	1.77	<0.05	<0.005	0.22	0.870
Ru/Pd low LHSV 24–30 h	82.09	12.40	3.43	1.80	<0.05	<0.005	0.08	0.846
Ru/Pd low LHSV 36–42 h	81.38	11.73	4.84	1.71	0.045	0.013	0.23	0.880
CoMoS high LHSV 4–5 h	79.86	10.78	0.40	1.60	<0.05	<0.005	0.20	0.835
CoMoS low LHSV 6–12 h	79.01	12.55	1.90	1.89	<0.05	<0.02	<0.01	0.792
CoMoS low LHSV 12–18 h	82.26	12.00	1.85	1.73	<0.05	<0.02	<0.01	0.835

Table 11. ¹³C 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

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. The balance of the catalyst beds were free-flowing and easily removed from the reactor tube for analysis.

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%. Because 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 8 and 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 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 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

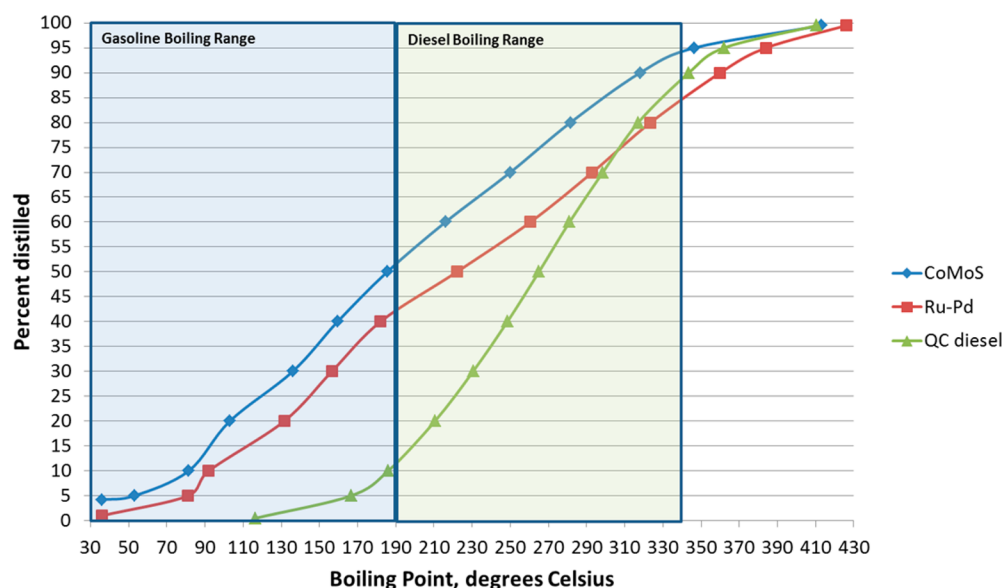


Figure 6. SimDist of hydrotreated red oak phenolic oil from low LHSV tests.

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.¹⁶

¹³C NMR analysis of the products also shows dramatic changes in carbon types (Table 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 24–30h) 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 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 nonsulfided 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 two-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 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.

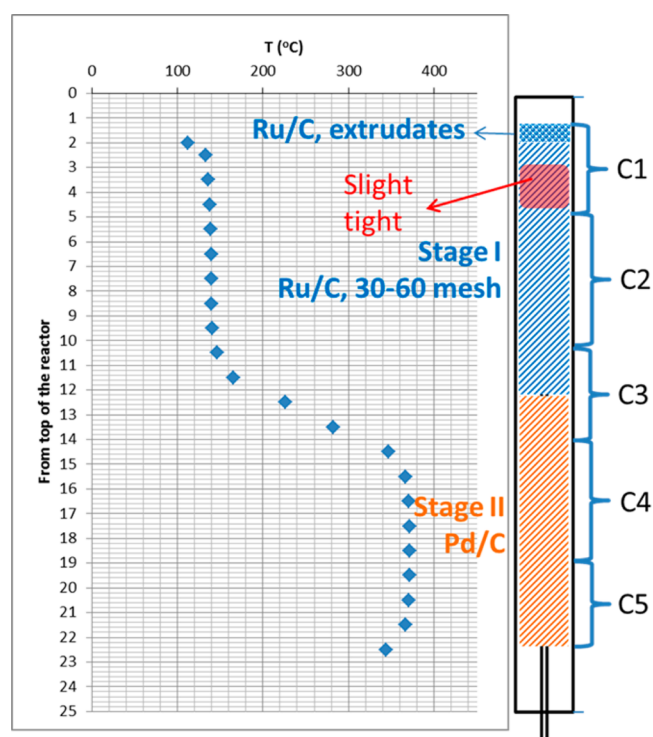


Figure 7. Schematic of the catalyst beds after use with corn stover phenolic oil.

The results for the corn stover phenolic oil hydrotreating test are given in Table 12 and the feed and product analyses are shown in Table 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

Table 12. Results from Hydroprocessing Corn Stover Phenolic Oil

TOS, h	mass yield, oil product, g dry/g dry feed	carbon yield, oil product, g C/g C in feed	oil product density, g/mL	gas yield, g per g dry feed	produced water yield, g per g dry feed	H ₂ consumed, g H ₂ /g dry feed	mass balance, %	carbon balance, %
24–30	0.533	0.632	0.825	0.128	0.221	0.045	91.8	80.0
36–42	0.580	0.679	0.857	0.111	0.215	0.040	94.6	82.7

Table 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

from a similar herbaceous feedstock, switchgrass, wherein the results are around 0.75.¹⁶

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.²¹ 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 up to 0.88 g/mL over the period of the longer tests, 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.

The product gas composition showed some interesting variations with catalyst, feedstock, and space velocity, as shown in Table 14. The composition is presented on a hydrogen-free basis and shows only the product gases. For these tests there was

Table 14. Product Gas Composition from Hydroprocessing Phenolic Oil, vol % (H₂-free Basis)

TOS, h	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	CO	CO ₂
red oak PdRe							
4–6 ^a	71.3	5.5	5.6	0.7	0	0	16.9
red oak Ru–Pd							
12–18 ^b	23.0	4.4	5.4	0	0	19.7	47.6
24–30 ^c	17.9	3.4	5.0	2.4	1.0	11.8	58.6
red oak CoMoS							
4–6 ^a	52.0	8.0	11.0	2.8	0.4	0	25.9
12–18 ^d	53.6	12.6	23.4	3.8	2.2	0	4.4
corn stover Ru–Pd							
24–30 ^c	11.9	6.3	55.2	2.2	0	9.8	14.6

^aHigh LHSV 0.5. ^bHigh LHSV 0.2/0.2. ^cLow LHSV 0.1/0.1. ^dLow LHSV 0.2.

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 isopropyl alcohol 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) whereas 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 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 amounts of K and S (see Table 5). Analysis of the catalyst bed fractions after the tests (see Table 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 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.¹⁶ In the catalyst bed of sulfided CoMo on Al₂O₃, the Ca is only reduced (at levels similar to Co, Mo, Al) by the dilution of

Table 15. Catalyst Analyses before and after Hydroprocessing Red Oak Phenolic Oil (ppm, Dry Basis)

	Ru/C fresh	used Ru/C		used Pd/C		Pd/C fresh	CoMo/Al ₂ O ₃ fresh	used CoMo/Al ₂ O ₃		
		C2 ^a	C3 ^a	C5 ^a	C6 ^a			C1 ^a	C2 ^a	C3 ^a
Al	695	1145	786	630	522	1040	386000	283900	314100	331450
Ca	417	262	157	192	367	484	987	740	842	931
Co	NA ^a	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

^aNumbering indicates different positions in catalyst bed, as shown in Figure 5. ^bNA = not analyzed.

Table 16. Catalyst Analyses before and after Hydroprocessing Corn Stover Phenolic Oil (ppm, Dry Basis)

	Ru/C fresh	used Ru/C			used Pd/C		Pd/C fresh
		C1 ^a	C2 ^a	C3 ^a	C4 ^a	C5 ^a	
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

^aNumbering indicates different positions in catalyst bed, as shown in Figure 7.

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 RuS₂ but it is lower than the fresh catalyst analysis. A typical level, based on literature reports, is 40% Ru sulfidation in a hydrothermal environment.²² 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 measurable in the red oak phenolic oil (see Table 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 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 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.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Bridgwater, A. V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94.
- (2) Lindfors, C.; Kuoppala, E.; Oasmaa, A.; Solantausta, Y.; Arpiainen, V. Fractionation of bio-oil. *Energy Fuels* **2014**, *28*, 5785.
- (3) Elliott, D. C. Historical developments in hydroprocessing bio-oils. *Energy Fuels* **2007**, *21*, 1792–1815.
- (4) Wang, H.; Male, J.; Wang, Y. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. *ACS Catal.* **2013**, *3*, 1047–1070.
- (5) de Miguel Mercader, F.; Koehorst, P. J. J.; Heeres, H. J.; Kersten, S. R. A.; Hogendoorn, J. A. Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. *AIChE J.* **2011**, *57* (11), 3160–3170. Ardiyanti, A. R.; Khromova, S. A.; Venderbosch, R. H.; Yakovlev, V. A.; Melián-Cabrera, I. V.; Heeres, H. J. Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. *Appl. Catal., A* **2012**, *449*, 121–130.
- (6) Zacher, A. H.; Olarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B. A review and perspective of recent bio-oil hydrotreating research. *Green Chem.* **2014**, *16*, 491–516.
- (7) Ben, H.; Mu, W.; Deng, Y.; Ragauskas, A. J. Production of renewable gasoline from aqueous phase hydrogenation of lignin pyrolysis oil. *Fuel* **2013**, *103*, 1148.
- (8) Mercader, F. dM.; Groeneveld, M. J.; Kersten, S. R. A.; Geantet, C.; Toussaint, G.; Way, N. W. J.; et al. Hydrodeoxygenation of pyrolysis oil fractions: Process understanding and quality assessment through co-processing in refinery units. *Energy Environ. Sci.* **2011**, *4*, 985.
- (9) Pollard, A. S.; Rover, M. R.; Brown, R. C. Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties. *J. Anal. Appl. Pyrol.* **2012**, *93*, 129–138.
- (10) 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. *J. Anal. Appl. Pyrol.* **2014**, *105*, 262–268.
- (11) 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.
- (12) Oasmaa, A.; Elliott, D. C. Process for stabilizing fast pyrolysis oil and stabilized fast pyrolysis oil. U.S. Patent US 20120285079 A1, November 15, 2012.
- (13) 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.
- (14) 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.
- (15) 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.
- (16) 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.
- (17) 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. *J. Anal. Appl. Pyrol.* **2013**, *104*, 194–201.
- (18) 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. Sustainable Energy* **2009**, *28* (3), 441–449.
- (19) Elliott, D. C.; Hart, T. R. Catalytic hydroprocessing of chemical models for bio-oil. *Energy Fuels* **2009**, *23*, 631–637.
- (20) Elliott, D. C.; Hart, T. R.; Hu, J.; Neuenschwander, G. G. Palladium catalyzed hydrogenation of bio-oils and organic compounds. U.S. Patent US 7425657 B1, September 16, 2008.
- (21) 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.
- (22) 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.