ACS Sustainable Chemistry & Engineering

Research Article

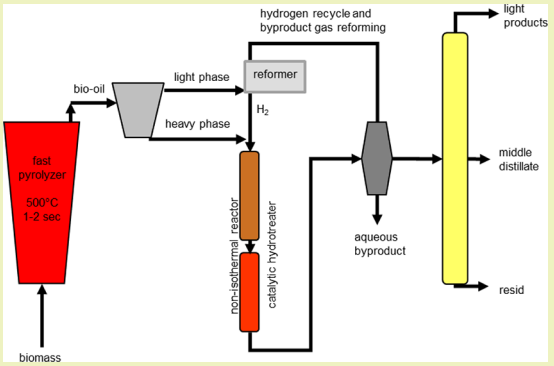
pubs.acs.org/journal/ascecg

Hydroprocessing Bio-Oil and Products Separation for Coke Production

Douglas C. Elliott,* Gary G. Neuenschwander, and Todd R. Hart

Pacific Northwest National Laboratory, P.O. Box 999, MSIN P8-60, Richland, Washington 99352, United States

ABSTRACT: Fast pyrolysis of biomass can be used to produce a raw bio-oil product, which can be upgraded by catalytic hydroprocessing to hydrocarbon liquid products. In this study, the upgraded products were distilled to recover light naphtha and oils and to produce a distillation residue with useful properties for coker processing and production of a renewable low-sulfur electrode carbon. For this hydroprocessing work, phase separation of the bio-oil was applied as a preparatory step to concentrate the heavier, more phenolic components, thus, generating a more amenable feedstock for residue production. Low residual oxygen content products were produced by continuous-flow catalytic hydroprocessing of the phase separated bio-oil.



KEYWORDS: *Biomass, Pyrolysis, Catalysis, Distillation residue*

INTRODUCTION

Biomass conversion technologies provide an option for production of renewable replacements for petroleum-derived products.[1] In particular, fast pyrolysis is a useful method for high yields of liquid products from biomass.[2] Although this type of processing work was initiated in the 1980s,[3] it is only recently (past 5 years) that the effort has been restarted in earnest because the price of petroleum has dramatically increased.[4,5] Although there have been several reviews of the field,[6−9] 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.[10] Although bio-oil is recovered as a single phase product, it can be separated into two phases by addition of water. Separation can also 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.[11] 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.

Catalytic hydroprocessing of bio-oil can be used to deoxygenate the raw bio-oil and generate liquid hydrocarbon products.[3] The product quality has been studied with the intent to determine potential uses, for example, as petroleum refinery feedstock.[12] In this study, we consider the distillation fractions of the upgraded product with an eye on distillation residue production for generating a low-sulfur renewable carbon electrode for metal refining.

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 streams of bio-oil and hydrogen gas (trickle-bed processing). A bench-scale unit with a 980 mL (1.5 in ID X 32 in long) fixed catalyst bed was used for the process tests. The system flowsheet is shown in Figure 1. The preheated 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 nonisothermal 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 that 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 were recovered manually as well as also logged to the data acquisition system. A LabView control and data acquisition software was used.

For the work discussed here, gas chromatography was the primary analytical tool. Gas chromatography in combination with a mass selective detector (GC-MS) was most useful to identify specific components in the hydrogenated product oils using a temperature program over the full operational range of the DB-5 column. Gas samples were routinely recovered manually and analyzed by gas

Received: September 27, 2012
Revised: November 27, 2012
Published: March 5, 2013

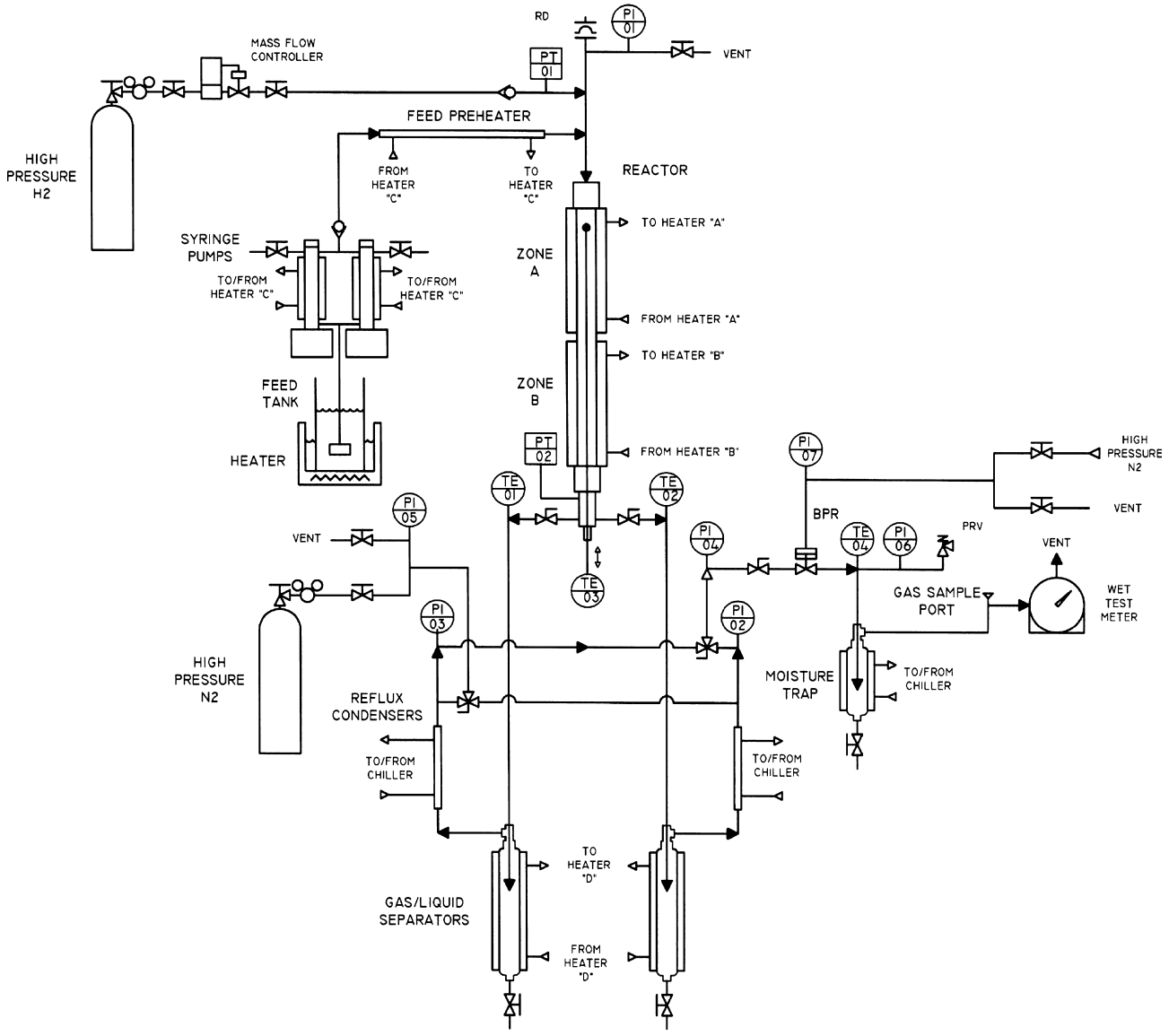


Figure 1. Schematic of bench-scale bio-oil hydroprocessing system.

chromatography using a Carle AGC as a dedicated gas analyzer. The AGC used two sets of columns with automatic switching controls to separate hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, oxygen, and nitrogen using a thermal conductivity detector, and higher hydrocarbons, up to C6, using a flame ionization detector.

Hydrogen was determined through the use of the Carle hydrogen transfer system, a metallic membrane for hydrogen separation by diffusion. The GC signal was processed, plotted, and integrated. A table of data including retention times, peak identifications, and gas composition based on previously analyzed standard gas mixtures was used. A 0.7 cm gas sample was used for analysis.

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/molybdenum on an 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 ditertiary-butyl-disulfide in 500 mL of decane was pumped through the catalyst bed at 0.1 liquid hourly space velocity (LHSV) for 1 h at 250 °C with a subsequent period of 3 h at 380 °C. Hydroprocessing temperature set points of 250 and 240 °C in the upper (first) bed and 390 and 380 °C in the lower (second) bed were used with a bio-oil feed rate of around 0.15 LHSV. The hydrogen flow was maintained at large excess of 1900 L/L bio-oil feed. A significant exothermic reaction caused portions of the catalyst beds to operate at 30 to 60 °C higher than the set points.

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.

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 spontaneously separated from the single-phase whole bio-oil during extended storage over a period of years and provided a convenient method to concentrate the higher-molecular weight and more aromatic components of the bio-oil. Because one goal of this study was to produce hydroprocessed bio-oil residue, the use of the heavy phase provided a more direct route to production of residue in a higher yield. The analysis of the heavy phase feedstock showed that it was significantly different from typical fast pyrolysis bio-oil, being

dx.doi.org/10.1021/sc300103y | ACS Sustainable Chem. Eng. 2013, 1, 389−392

lower in oxygen content and water, as has been reported elsewhere.[4] These tests proceeded smoothly with all reactor components functioning as designed. The process data are summarized in Table 1.

Table 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	269	273	272
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

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 30−40 h in a similarly dimensioned vessel.[4] 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 period, but the deposits were attributed to an inappropriate restart procedure (resulfiding the catalyst bed without previously washing out the residual bio-oil with acetone). The first two periods were made with the same catalyst bed, and the third and fourth were made with the same catalyst bed, which was composed of the period 1−2 bed with some of the fouled catalyst replaced with fresh catalyst. Appropriate shutdown was determined to include a hot acetone rinse of the catalyst bed, and the catalyst was resulfided prior to restart. Excessive 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,[4] the operating conditions were quite similar, considering the exothermic reaction and 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 derivatives (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 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.

Table 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 g/mL	1.25	0.87	0.89	0.90

Distillation Processing of the Hydroprocessed Products. The 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 nonvolatile 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 at 22 °C. The remainder amounted to 4544 g with a density of 0.96 g/mL at 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.

Table 3. Hydroprocessed Bio-Oil Fraction analyses

	rotavap	vacuum distillate	high-temp. distillate	distillation residue
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

Thermogravimetric Analysis (TGA) was applied to the residue to approximate the yield of coke that could be recovered for electrode production. The analysis of this residue shows that it is a low sulfur and low oxygen material with a high aromatic content suggested by the hydrogen to carbon atomic ratio approaching 1. Solid state carbon-13 nuclear magnetic resonance spectrometry of a sample of the residue provided further confirmation. Integration of that spectra showed a 71/29 split of aromatic (114−155 ppm chemical shift range) to aliphatic (10−48 ppm) for the carbons responding in the scan. TGA recovered 19 wt % of nonvolatile "coke" after heating to 700 °C at 50 °C per minute. TGA of the vacuum and high-

dx.doi.org/10.1021/sc300103y | ACS Sustainable Chem. Eng. 2013, 1, 389−392

Table 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- and p-cresol	2.26
methylcyclohexane	3.98	ethylbenzene	1.80	o-cresol	1.20
methylcyclopentane	2.03	m- and 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- and 4-ethyl phenol	0.88
hexane	1.18	trimethylbenzene	0.92	propyl phenol	0.54

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. On the basis of 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.[12] 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 10−15% of the distillate and included phenol and all three methyl- and ethyl-isomers, as well as C_3-phenols like methyl−ethyl compounds and propyl phenol. The major components are listed in Table 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 is only approximate.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dougc.elliott@pnnl.gov.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The support for preparation for publication of this article was provided by the Bioenergy Technologies Office of the U.S. Department of Energy. Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under contract AC0676RLO1830.

REFERENCES

(1) Yaman, S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manage.* **2004**, *45*, 651−671.

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

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

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

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

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

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

(8) Venderbosch, R. H.; Prins, W. Fast pyrolysis technology development. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 178−208.

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

(10) 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.

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

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