

Field-to-Fuel Performance Testing of Lignocellulosic Feedstocks: An Integrated Study of the Fast Pyrolysis–Hydrotreating Pathway

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ABSTRACT: Feedstock composition can affect final fuel yields and quality for the fast pyrolysis and hydrotreatment upgrading pathway. However, previous studies have focused on individual unit operations rather than the integrated system. In this study, a suite of six pure lignocellulosic feedstocks (clean (no bark) pine, whole-tree (including bark) pine, tulip poplar, hybrid poplar, switchgrass, and corn stover) and two blends (equal weight percentages whole-tree pine/tulip poplar/switchgrass and whole-tree pine/clean pine/hybrid poplar) were prepared and characterized. These materials then underwent fast pyrolysis and hydrotreatment. Although some feedstocks showed a high fast pyrolysis bio-oil yield, such as tulip poplar at 60%, high yields in the hydrotreater were not always observed. Results showed overall fuel yields of 17% (switchgrass), 20% (corn stover), 24% (tulip poplar, blend 1, blend 2), 25% (whole-tree pine, hybrid poplar), and 27% (clean pine). Simulated distillation of the upgraded oils indicated that the gasoline fraction varied from 39% (clean pine) to 51% (corn stover), while the diesel fraction ranged from 40% (corn stover) to 46% (tulip poplar). Little variation was seen in the jet fuel fraction at 11–12%. Hydrogen consumption during hydrotreating, a major factor in the economic feasibility of the integrated process, ranged from 0.051 g/g dry feed (tulip poplar) to 0.070 g/g dry feed (clean pine).

1. INTRODUCTION

Fast pyrolysis followed by bio-oil upgrading into a hydrocarbon blendstock is considered to be a near-term opportunity for the production of biofuels¹ that could mitigate the impact^{2–4} of petrochemical transportation fuels, a sector that accounts for 70% of all petroleum consumption in the United States.⁵ Understanding conversion performance as a function of feedstock properties is a critical element of both the design and successful operation of an integrated biorefinery. In addition, this understanding would allow for commoditization of biomass, allowing producers to optimize quality versus quantity trade-offs for specific feedstocks. To date, several studies have investigated the yields of bio-oil from fast pyrolysis and reported liquid mass yields ranging from 36 to 62% (dry basis).^{6–9} The yield of upgraded hydrocarbon fuels from these bio-oils is being studied but remains far less understood.^{10,11} The wide range of reported yields coupled with unknown upgrading performance presents a challenge for the bioenergy industry in successfully designing and operating a fast pyrolysis biorefinery. To address this challenge the Idaho National Laboratory (INL), National Renewable Energy Laboratory (NREL), and Pacific Northwest National Laboratory (PNNL) began a detailed performance study dubbed “Field to Fuel” to integrate and examine feedstock conversion from harvest through hydrocarbon blendstock production.

Fast pyrolysis is a thermochemical, direct liquefaction process in which a biomass feedstock is rapidly heated in an inert environment at temperatures ranging from 450 to 550 °C to produce a mixture of vapors and liquid aerosols (bio-oil), solids (char), and noncondensable gases such as CO₂, CO, and CH₄.¹² As stated above, reported organic liquid yields (not including water) range from a low of 36% to a high of 62%. Possible reasons

for the wide range of liquid yields include variation in the amount of total ash present in the feedstock, amounts of specific inorganic compounds such as alkali and alkali earth metals, syringyl/guaiacyl (S/G) ratios of the feedstocks, and processing conditions such as temperature, residence time, and particle size.¹³ Raw fast pyrolysis oil is corrosive and thermally unstable, so it significant challenges for blending or direct insertion into refinery operations at levels greater than 5%.¹⁴ Therefore, raw fast pyrolysis bio-oil typically is considered to be an intermediate product that can be upgraded via processes such as catalytic hydrogenation, hydrotreating, and hydrocracking. Hydroprocessing removes the oxygen-rich functional groups responsible for undesirable bio-oil characteristics in a high-pressure (~20 MPa) catalytic reactor operated at elevated temperatures (~400 °C). Studies by Elliot and co-workers show that the degree of deoxygenation is dependent on process severity, with higher temperatures and higher H₂ pressures capable of almost complete (99.5%) deoxygenation.¹⁵

Because different feedstocks exhibit varying overall conversion performance to hydrocarbon blendstocks, development of a commodity style grading of biomass based on conversion performance specifications could enable and accelerate commoditization of biomass. Techno-economic analysis performed by Jones et al.¹⁶ has shown that the delivery of “on-spec” feedstocks remains the single largest operating cost component, contributing 0.92 \$/GGE, compared to 0.32 \$/GGE for catalysts and chemicals. The Jones analysis also points out that feedstock cost

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is the third highest overall risk factor for biomass-to-fuel processes, behind total plant size and the internal rate of return. To meet the U.S. Department of Energy's biofuel production and cost goals, high-volume and potentially diverse biomass types will need to be included in the biomass supply chain.¹ To identify the types of biomass available in the United States that could potentially contribute to biofuels, the Billion Ton Study was initiated jointly by the Department of Energy and the U.S. Department of Agriculture in 2005¹⁷ and then updated in 2011 to address costs and quantities.¹⁸

Although a steady and uniform supply of biomass feedstocks is essential to any conversion facility, how the biomass behaves through the entire conversion process is equally important. Because of the intense capital and technical requirements, results from integrated studies focused on the effect of biomass compositional parameters on the fast pyrolysis bio-oil and the upgraded blendstock are not available in the literature. Many studies have explored the effect of different biomass parameters on bio-oil yield,^{19–21} while other studies have explored how bio-oil characteristics affect hydrotreatment behavior.^{10,22} However, these studies have not attempted to characterize the entire process; rather, they have focused on individual unit operations, such as fast pyrolysis or hydrotreatment.

In this joint study, eight different feedstocks—including six pure feedstocks and two blends—were prepared and characterized at INL. The feedstocks then were processed via fast pyrolysis at NREL to generate bio-oils that were subsequently characterized. The bio-oils were then hydrotreated at PNNL to generate an upgraded hydrocarbon fuel blendstock. This blendstock was characterized and analyzed to determine overall yields from feedstock to upgraded fuel, as well as potential fuel product distributions (gasoline, diesel, jet fuel). The results described here provide detailed data for technoeconomic analysis, life-cycle analysis, and process development parameters for converting biomass feedstocks to upgraded biofuels.

2. EXPERIMENTAL SECTION

2.1. Feedstocks. The biomass varieties chosen for this study include specific types identified by the Billion Ton Update¹⁸ as being available in large quantities (>50 million tons/year combined) that could be potentially blended and delivered at a cost approaching \$80/dry ton. They include clean (i.e., with all bark removed) pine (*Pinus taeda*) provided by Corley Land Services, harvested 2013 in Butler, Alabama; whole-tree (i.e., with bark remaining) pine (*Pinus taeda*) also provided by Corley Land Services, harvested 2013 in Butler, Alabama; hybrid poplar (*Populus x euramericana*) provided by Greenwood Resources harvested 2013 in Morrow, Oregon; tulip poplar (*Liriodendron tulipifera*) provided by Patterson Chip Company, harvested 2014 in Knox, Kentucky; corn stover (*Zea mays*) provided by the Idaho National Laboratory, harvested 2011 in Boone, Iowa; and switchgrass (*Panicum virgatum*) provided by Oklahoma State University, harvested 2012 in Garvin, Oklahoma. The clean pine and whole-tree pine were selected because those materials are generally expected to have important and perhaps dominant roles in biofuels production via thermochemical conversion pathways. Switchgrass was selected because it is expected to be important in order for thermochemical conversion processes to achieve volume targets set by congressional mandates in the United States.²³ Corn stover was selected as a second widely available herbaceous material. Hybrid poplar and tulip poplar were selected as representative hardwoods with very different syringal/guaiacol (S/G) ratios in lignin. Two blends were also prepared. Blend 1 consisted of equal weight proportions of the whole-tree pine, tulip poplar, and switchgrass mentioned above. Blend 2 consisted of equal weight proportions of the whole-tree pine, clean pine, and hybrid poplar mentioned above. The blends were selected to test a relatively clean

all-wood blend and a very different blend containing a herbaceous material with high inorganic content.

2.2. Feedstock Characterization. Compositional analyses, including total ash, structural and nonstructural inorganics, structural and nonstructural protein, water and ethanol extractives, sucrose, lignin, glucan, xylan, galactan, arabinan, mannan, and acetyl were performed at NREL following the standard *Laboratory Analytical Procedures for Biomass Compositional Analysis*.²⁴

Proximate, ultimate, and elemental ash analyses of the raw biomass samples were carried out by INL. Unless otherwise noted, samples were first ground to 2 mm grind size using a knife mill (Thomas Wiley Laboratory Mill Model 4, 1 hp; Thomas Scientific, NJ) and then ground using a Retsch ZM200 centrifugal mill grinder (Retsch, Haan, Germany) with a 0.2 mm screen. A thermogravimetric method using ASTM Standard D 5142 was used for proximate analysis with a LECO TGA701 (LECO, St. Joseph, MI). Ultimate analysis (CHN) of the feedstocks was conducted using a modified ASTM Standard D 5373 method (Flour and Plant Tissue Method) that used a slightly shorter burn profile with a LECO TruSpec CHN Analyzer (LECO, St. Joseph, MI). Elemental sulfur content was determined using ASTM Standard D 4239-10 and a LECO TruSpec S Analyzer (LECO, St. Joseph, MI), and oxygen content was determined by difference. Heating values (higher heating value [HHV] and lower heating value [LHV]) were determined with a LECO AC600 calorimeter (LECO, St. Joseph, MI) using ASTM Standard D 5865-10. Ash composition was analyzed at two grind sizes. First, samples were analyzed at 0.2 mm grind size prepared as described above, and second, samples were further ground using a 0.08 mm screen in the same Retsch grinder. The ash composition of the duplicate samples was measured at Huffman Laboratories Inc. (Golden, CO) after the samples were subjected to drying overnight at 60 °C and then stage ashing at 750 °C for 8 h. Reported results are the average of the duplicate measurements at different grind sizes.

Syringol/guaiacol ratios were determined using a pyrolysis molecular beam mass spectrometry system that was described previously,²⁵ and the methodology for the S/G ratio determination is described in Sykes et al.²⁶ Small samples (~40 mg) of each feedstock were pyrolyzed in triplicate at 500 °C under He using a quartz flow reactor.²⁶ A portion of the evolved gases and vapors was extracted through a critical flow sampling orifice into a custom-built, three-stage vacuum system and then analyzed using a commercial mass spectrometer. Mass spectra were recorded once per second while samples were introduced approximately every 2 min.

2.3. Fast Pyrolysis Processing. Bio-oils were produced using a 5 cm fluidized bed reactor system (2FBR). A schematic of the 2FBR system is shown in Figure 1. Biomass (<2.0 mm) was pyrolyzed in a bed of silica sand (300 to 500 μm), fluidized with 14 standard L/min of nitrogen. The bed was indirectly heated with a furnace to 500 °C, and the temperature was measured at three points vertically, all of which typically were within 10 °C of the temperature set point. Biomass was fed with an auger into the fluidized bed 2 cm above the gas distributor plate. Typical biomass feed rates were 400 g/h and totaled roughly 2 kg for each experiment, with the goal of producing ~1 L of oil for subsequent hydroprocessing tests. Char exiting the bed was removed in the solids cyclone, and remaining fine particles were removed downstream using an inline hot vapor filter (1 μm 316-SS pleated stainless steel screen). All lines, the cyclone, and the filter were heat traced and kept at approximately 400 °C.

Liquid products were condensed using a three-stage condensation train, the first of which was an air-cooled condenser cooled by simple convection. Condensed liquids were allowed to flow into an ice-cooled, two-neck flask. Gas and aerosols leaving the flask entered a 5 cm diameter electrostatic precipitator (ESP). The ESP was operated with a 5 kV potential on the central conductor and also was kept at ambient temperature by air cooling. Liquids collected in the ESP were drained as needed into a 1 L sample bottle, while the effluent passed into a coldfinger dry ice trap. All parts of the condensation train were weighed to obtain a raw oil yield, and the collected liquids were combined into the 1 L bottle and brought to room temperature. The bottle was then shaken so a homogeneous sample could be obtained for analysis. This process was acceptable for all bio-oils except for the corn stover oil,

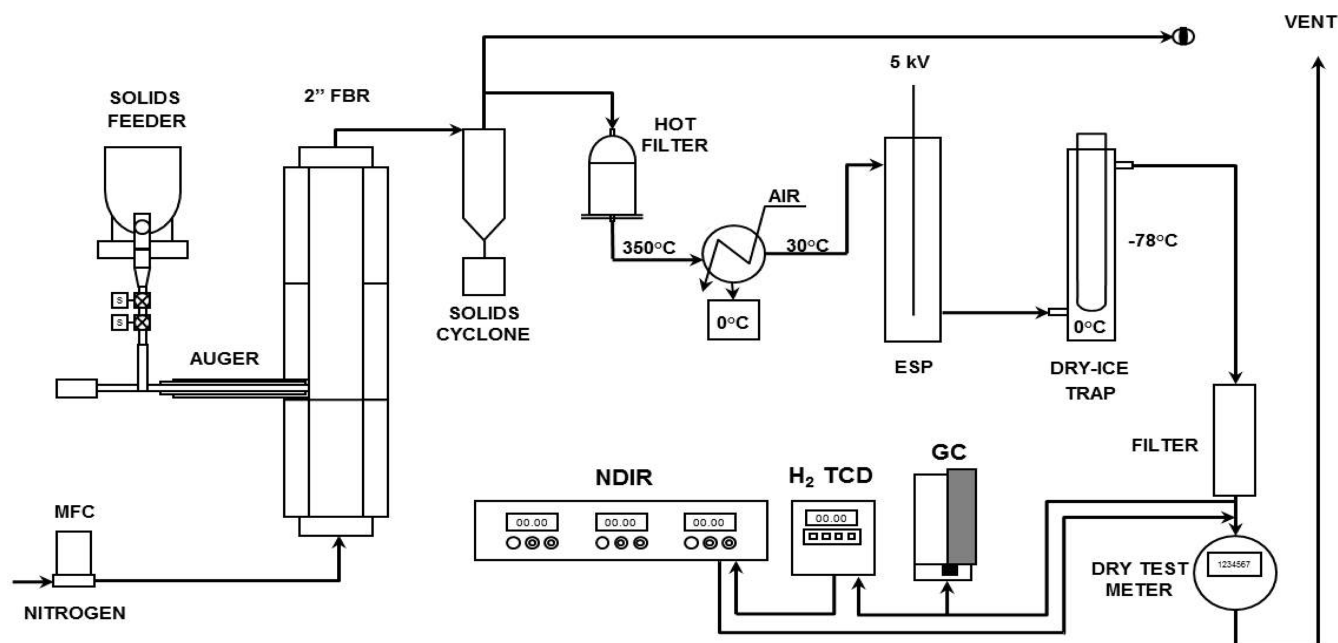


Figure 1. Process flow diagram of 2FBR system used for generating fast pyrolysis bio-oil.

which remained distinctly in two phases. For the corn stover oil, the top aqueous phase was decanted and analyzed separately from the bottom oil phase.

Gases leaving the dry ice trap were sent to 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 CH_4 , CO , and CO_2 modules was used to monitor the effluent gas in real time, as was a Thermal Conductivity Monitor TCM H_2 detector. A three-channel (MS-SA \times 10 m, PBQ \times 10 m, and CP-Sil 5 \times 8 m) Varian CP 4900 Micro-GC was used to measure permanent gases and C_2 and C_3 hydrocarbons.

2.4. Fast Pyrolysis Product Characterization. Proximate analyses were performed on the char and bio-oil using the same methods described above for the raw feedstocks. CHN/S content was measured using a LECO TruSpec CHN/S module with oxygen determined by difference.

The water content of the bio-oil was determined by Karl Fisher (KF) titration (ASTM Standard D 5530). Samples were vigorously shaken for 60–90 s to suspend any heavy material that had settled back into the oil. Approximately 100 μL of each oil sample was transferred to the KF titrator (Metrohm 701 Titrino), which was preconditioned to an anhydrous condition and titrated to the instrument end point. Each sample was measured in triplicate. Prior to titration, the KF reagent was standardized against a National Institute of Standards and Technology traceable water standard.

Bio-oil viscosity was determined using a Brookfield DV2T viscometer with a CPAS2Z spindle. Samples were shaken for 60–90 s to suspend any heavy material. The oil was drawn into a syringe, and a \sim 0.5 mL sample was passed through a 0.47 μm filter and placed into the sample cup of the viscometer. The spindle revolutions per minute was adjusted to provide a constant torque ($25 \pm 5\%$ of full scale) to the sample. After conditioning the sample at $24 \pm 1^\circ\text{C}$ for 2 min, the viscosity reading was taken using a 3 min average. Each sample was measured in triplicate. Prior to measurement of the first sample, instrument performance was checked against a viscosity standard.

The acid content or total acid number (TAN) of the oils was determined by automated titration using a Metrohm 905 Titrando titrator. Samples were shaken for 60–90 s to suspend any heavy material. Approximately 0.5 mL of oil was dissolved in 60 mL of ethanol and titrated against 0.5 M NaOH aqueous solution. The titration rate was adjusted automatically to limit the rate of pH change to 20 mV/min, thus providing adequate equilibration time. The NaOH solution was standardized against a potassium acid phthalate standard, and the

instrument performance was verified by titrating a known weight of 2-methoxy-benzoic acid in ethanol.

2.5. Hydrotreatment and Analysis. The eight pyrolysis oils generated at NREL were upgraded at PNNL in a two-stage hydrotreater to produce a refinery-ready fuel. A process flow diagram is shown in Figure 2. The hydrotreater had an inner diameter of 1.3 cm and an

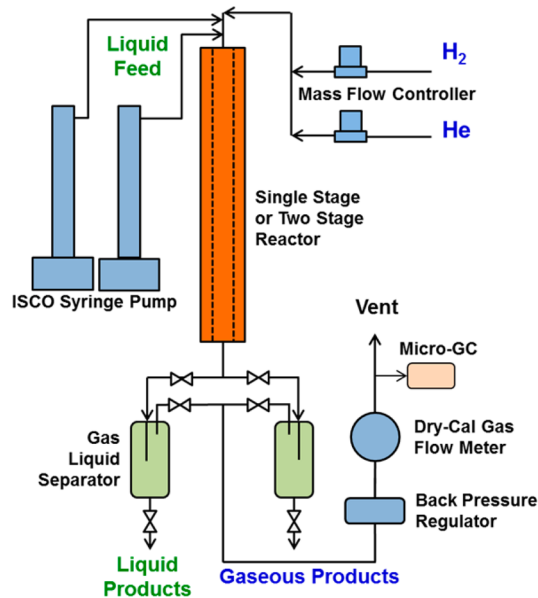


Figure 2. Process flow diagram of the two-stage hydrotreater used to upgrade the fast pyrolysis bio-oils. Prior to each run the catalysts are sulfided by feeding di-*tert*-butyl-disulfide to the reactor via the ISCO syringe pumps.

overall length of 63.5 cm. The first stage utilized a ruthenium catalyst on a carbon support. This catalyst was 7.8 wt % Ru prepared by impregnating ruthenium nitrosyl nitrate (purchased from BASF) on washed Norit ROX 0.8 C_E (purchased from Sigma-Aldrich) using an incipient wetness procedure. At the reactor inlet, 2 g of the Ru/C extrudates were loaded as a “guard bed” to prevent plugging. This is necessary because of the nonisothermal zone at the reactor inlet, which

can result in bio-oil polymerization. By adding the extrudates there is enough catalyst activity to prevent polymerization, but the lower active site density combined with the overall LHSV results in a negligible conversion contribution from the guard bed. From 5 to 32 cm within the reactor, ~13.6 g of +30–60 mesh Ru/C was loaded. This reactor zone was kept at 220 °C and 10.7 MPa (1550 psi). The second zone, located at 32–64 cm, utilized a cobalt/molybdenum catalyst on an alumina support (cobalt oxide 3.4–4.5%, molybdenum oxide 11.5–14.5%, on alumina, purchased from Alfa Aesar). Approximately 15.7 g of the catalyst was loaded in this zone, which was operated at 400 °C and 10.7 MPa (1550 psi). Prior to every experiment, the catalysts were sulfided by feeding di-*tert*-butyl-disulfide to the reactor for approximately 12 h via the ISCO syringe pumps seen in Figure 2. The fast pyrolysis oil was fed to the reactor using a syringe pump. In the case of corn stover, where the liquid condensate had both an organic fraction and a distinct aqueous fraction, the aqueous phase was fed to the reactor using a separate pump. The flow rates of each fraction were set to equal the ratio of oil/aqueous produced in the NREL 2FBR. The total liquid flow rate for all experiments was 48 mL/h. H₂, in stoichiometric excess, and He were fed to the top of the reactor along with the bio-oil. The liquid products exiting the reactor were collected and sampled every 6 h, while the gaseous products passed through a Dry-Cal flow meter and were analyzed using an Agilent 3000A Micro-GC. The Dry-Cal flow meter and the gas chromatograph were operated continuously.

Liquid samples generated from hydrotreatment consisted of an aqueous layer and an organic (oil) layer. These two layers were highly distinct and easily separated gravimetrically. The two fractions were weighed, and the density of the oil phase was calculated. Steady-state operation was defined as the period during which the density of the product oil did not change. At the end of each experiment, the yields to the various phases (oil, aqueous, and gas) were calculated. Subsamples of the oil from the steady-state period were collected for analysis. ALS Environmental in Tucson, Arizona, analyzed the samples for CHNO/S, TAN, LHV, HHV, and water by Karl Fischer titration. Simulated distillation was performed at PNNL following ASTM Standard D 2887. A nonpolar column (BPX1 from SGE Analytical Science) was used in an Agilent 6890N gas chromatograph with He as the carrier gas. The oven temperature was ramped from 35 to 350 °C at 20 °C/min. Prior to each run the GC was calibrated using a standard mixture of *n*-alkanes (*n*-paraffin) from C₅ to C₄₄ purchased from AC Analytical Controls Inc., with the retention times calibrated with respect to their reported boiling point. Samples are analyzed and the Simulated Distillation software (Chemstation) integrates the chromatograms by area slices rather than peak integration. The area slices are quantified for mass percent with respect to the total area summation of the chromatogram, and the mass percent is reported with respect to boiling point. The results from the simulated distillation were further analyzed by fitting the mass loss as a function of temperature data to a sixth-order polynomial to determine the fraction of the compounds that boil in the gasoline, diesel, and jet fuel ranges. The remainder was then classified as “heavies.” Inorganic analysis of the oil and aqueous fractions was performed via inductively coupled plasma–optical emission spectrometry. Approximately 0.2 g of the oil was weighed into a microwave digestion vessel, and 10 mL of concentrated nitric acid was added. It was then heated in a sealed vessel to 210 °C, held for 30 min, and cooled. The sample was then quantitatively transferred and diluted to 50 mL. Aqueous fractions were analyzed as received. The instrument used was a PerkinElmer Optima 7300DV Optical Emission Spectrometer, configured with a Meinhard nebulizer, glass cyclonic spray chamber, and 2.0 mm alumina injector. Calibration standards were prepared from certified standards and verified with certified standards from a second source. Calibration standards and quality control standards were analyzed daily. Samples were diluted in deionized water as necessary to be within the calibration range. The elements analyzed were Ag, Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Re, Sr, V, Y, Zn, Mo, Si, Ti, W, Au, Pd, Pt, Rh, Ru, S, Sn, and Zr. Only elements of interest are reported in this publication.

3. RESULTS AND DISCUSSION

3.1. Feedstock Characterization. Tables 1 and 2 summarize the chemical composition, fuel properties (ultimate

Table 1. Raw Feedstock Properties from Compositional Analysis Reported on a Dry Basis^a

(%)	Cl-Pn	Wh-Pn	Hy-Pop	Tu-Pop	Cn-St	Sw-Gr
total ash	0.71	0.70	0.91	0.46	4.27	4.20
structural inorganics	0.64	0.56	0.98	0.46	2.33	2.23
non-structural inorganics	BDL	BDL	BDL	BDL	1.97	1.61
total protein	0.28	0.28	0.37	0.37	2.16	1.29
structural protein	0.22	0.22	0.31	0.27	1.35	1.02
non-structural protein	0.05	0.05	0.06	0.10	0.82	0.27
sucrose	BDL	BDL	BDL	BDL	0.22	3.62
water extractable others	BDL	0.12	0.23	BDL	4.43	3.51
ethanol extractives	3.63	3.15	3.54	2.77	2.52	2.23
lignin	31.72	32.09	25.95	26.72	16.80	17.32
glucan	39.69	39.25	45.31	42.73	36.34	34.88
xylan	6.97	6.97	13.24	15.67	23.74	23.65
galactan	2.39	2.36	1.34	1.35	1.57	1.32
arabinan	1.46	1.38	0.14	BDL	2.99	2.70
mannan	9.88	9.90	2.79	5.01	0.18	0.16
acetyl	1.47	1.58	3.84	3.59	1.50	2.51
total %	98.20	97.78	97.66	98.67	96.72	97.39

^aAbbreviations in this and subsequent tables are as follows: Cl-Pn, clean pine; Wh-Pn, whole-tree pine; Hy-Pop, hybrid poplar; Tu-Pop, tulip poplar; Cn-St, corn stover; Sw-Gr, switchgrass; BDL, below detectable limits.

and proximate analyses), inorganic content, and S/G ratios of the feedstock materials. As expected, the herbaceous materials contain much higher concentrations of inorganics and structural proteins and lower levels of lignin than the woody materials. Other results of interest are that the ash and fixed carbon contents of the tulip poplar were lower than those of the other feedstocks, and the S/G ratios of the tulip and hybrid poplars were significantly higher than those of the other feedstocks. Relative to the other woody materials, the hybrid poplar had high calcium and potassium contents.

3.2. Pyrolysis Product Characterization. Table 3 summarizes the composition of the liquid, solid, and gas product fractions observed during fast pyrolysis experiments. Notably, the herbaceous materials exhibited lower CO and higher CO₂ generation compared to the woody materials. Corn stover and tulip poplar had the highest (22.3 wt %) and lowest (13.5 wt %) total gas yields, respectively. Table 3 also contains the results of chemical analyses performed on the pyrolysis char and liquid fractions. The char from the herbaceous materials contained lower carbon concentrations and higher ash concentrations than the woody materials. The carbon content of the pyrolysis oils from the herbaceous materials also was lower than those of the woody feedstocks, while the nitrogen and oxygen contents from the herbaceous materials were higher than those of the woody feedstocks. The switchgrass and the blend containing switchgrass exhibited the highest TANs, followed by the hybrid poplar and tulip poplar. The tulip poplar exhibited oil yield (73.9 wt %) significantly higher than that of the other materials. This compares to a maximum oil yield of 68.5 wt % when using yellow poplar as the feedstock as reported by Kim et al.,²⁷ indicating that

Table 2. Raw Feedstock Properties from Proximate, Ultimate, Calorific, and Elemental Ash Analysis Reported on a Dry Basis^a

	Cl-Pn	Wh-Pn	Hy-Pop	Tu-Pop	Cn-St	Sw-Gr	blend 1	blend 2
ash (%)	0.71	0.70	0.91	0.46	4.27	4.20	1.66	0.62
vol. matter (%)	85.0	83.9	84.9	88.2	79.0	80.2	82.6	84.8
fixed C (%)	14.3	15.4	14.2	11.4	16.7	15.6	15.7	14.6
HHV (BTU/lb)	8614	9063	8561	8519	7990	8077	8473	8873
LHV (BTU/lb)	7269	7728	7199	7151	6614	6749	7111	7504
C (%)	49.6	50.2	49.9	49.2	48.7	47.2	49.3	50.4
H (%)	5.9	5.9	5.8	5.8	5.7	5.7	5.9	5.9
N (%)	0.2	0.2	0.2	0.2	0.7	0.5	0.3	0.2
S/G ratio	0.13	0.14	1.21	2.32	0.56	0.54	0.83	0.35
Al (ppm)	199	184	76	39	62	60	89	106
Ca (ppm)	942	1094	1703	934	2810	2312	1359	1153
Fe (ppm)	293	424	142	62	354	538	383	143
Mg (ppm)	266	290	377	258	1598	2580	929	293
Mn (ppm)	68	73	7	35	32	65	57	48
P (ppm)	75	93	252	70	551	830	317	133
K (ppm)	757	754	1956	813	9325	6090	2495	1129
Si (ppm)	1555	1293	524	562	10043	10848	3627	667
Na (ppm)	51	54	79	23	25	504	182	49
S (ppm)	68	73	107	69	386	465	180	78
Ti (ppm)	13	10	7	3	3	4	6	6

^aThe syringal/guaiacol (S/G) ratio determined by pyrolysis molecular beam mass spectrometry also is included. All numbers are reported on dry feedstock basis.

Table 3. Pyrolysis Product Characterization Including Liquid, Solid, and Gas Fractions

	Cl-Pn	Wh-Pn	Hy-Pop	Tu-Pop	Cn-St	Sw-Gr	blend 1	blend 2
Liquid Fraction								
C (wt %)	45.0	45.3	45.9	44.8	37.2	35.1	40.1	43.0
H (wt %)	7.8	8.1	8.1	7.7	9.1	9.0	8.5	8.4
N (wt %)	0.08	0.09	0.08	0.08	0.7	0.36	0.19	0.09
O (wt % calcd.)	47.1	46.5	45.9	47.4	52.9	55.4	50.3	48.4
S (wt %)	0	0	0	0	0	0	0	0
water (wt %)	21.1	22.5	20.7	18.8	40.0	37.0	27.1	25.9
TAN (mg/g KOH)	39.6	37.9	65.5	70.8	43.8	104.3	71.5	47.3
viscosity (cP, 25 °C)	83.4	92.2	59.5	101	400.2	16.6	38.7	44.4
tot. carbon (wt % biomass C)	60.7	57.9	62.1	67.3	46.9	46.2	54.4	53.5
total liquid yield (wt % dry biomass)	66.9	64.2	67.5	73.9	56.2	62.1	66.9	62.7
Al (ppm)	1.2	1.4	2.4	1.9	1.6	1.8	1.1	3.2
Ca (ppm)	4.5	4.7	7.6	41.0	29.2	48.6	48.2	43.1
Fe (ppm)	BDL	2.5	BDL	BDL	1.2	0.5	0.6	0.6
K (ppm)	BDL	BDL	BDL	BDL	14.8	BDL	BDL	27.2
Mg (ppm)	0.9	0.8	1.2	7.7	5.1	8.7	8.8	7.9
Na (ppm)	BDL	BDL	BDL	7.2	5.5	7.9	8.4	10
P (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S (ppm)	37.2	41.1	56.3	48.3	486.9	239.7	112.1	49.8
Char Fraction								
C (wt %)	75.8	80.9	77.8	74.6	54.7	61.9	72.6	80.1
H (wt %)	5.0	4.2	4.2	4.1	2.6	3.6	4.8	5.3
N (wt %)	0.2	0.2	0.3	BDL	BDL	BDL	0.5	0.3
O (wt % by difference)	13.6	8.9	10.1	13.6	24.8	14.5	10.4	10.3
S (wt %)	0.04	0.06	0.05	0.06	0.07	0.15	0.08	0.04
Ash (wt % dry)	5.37	5.76	6.05	7.53	17.85	19.69	11.74	3.99
% tot. carbon (wt % biomass C)	24.2	13.9	14.2	11.6	21.4	21.4	11.8	23.7
% char yield (wt %)	12.0	15.0	8.9	7.6	19.1	10.8	7.3	13.3
Nitrogen-Free Gas Fraction								
CO (%)	40	40	34	42	27	31	36	39
CO ₂ (%)	46	46	55	45	62	58	52	47
CH ₄ (%)	8	8	6	7	6	6	7	8
C ₂₊ (%)	5	5	4	5	4	4	4	4
% tot. carbon (wt % biomass C)	11.9	12.4	12.4	9.3	14.2	12.2	13.8	14.8
% gas yield (wt %)	17.9	18.9	19.2	13.5	22.3	18.1	19.2	20.4

Table 4. Average of the Steady-State Yield Values on a Dry Fast Pyrolysis Oil (KF Subtracted Out) Feed Basis^a

	Cl-Pn	Wh-Pn	Tu-Pop	Hy-Pop	Cn-St	Sw-Gr	blend 1	blend 2
avg. upgraded oil yield (g oil/g dry feed- %)	51.5	50.1	40.1	46.0	56.8	41.6	49.5	51.9
avg. produced water yield (g H ₂ O/g dry feed, %)	34.7	35.7	36.2	36.9	36.0	34.5	37.3	34.3
avg. gas yield (g gas/g dry feed, %)	15.2	14.1	19.1	17.2	16.9	21.0	17.3	17.1
mass balance (g products/g dry feed,%)	101.5	99.8	95.5	100.1	109.7	97.2	104.0	103.4
fast pyrolysis oil yield (g dry oil/g dry biomass, %)	53.1	50.1	60.3	54.0	35.4	40.8	49.6	46.7
field-to-fuel yield (g fuel oil/g dry biomass, %)	27.4	25.1	24.2	24.9	20.1	17.0	24.5	24.3
field-to-fuel yield (g fuel oil C/g dry biomass C, %)	47.8	43.4	42.1	42.8	33.7	30.1	42.7	41.7

^aMoisture content of the biomass feedstock was subtracted so that all values are reported on a dry mass basis.

Table 5. Characterization of the Liquid Products from the Hydrotreater

	Cl-Pn	Wh-Pn	Tu-Pop	Hy-Pop	Sw-Gr	Cn-St	blend 1	blend 2
Oil Phase								
C (wt %)	87.15	87.52	86.05	86.76	87.3	85.3	87.18	87.05
H (wt %)	12.52	12.67	11.99	12.42	12.94	12.89	12.64	12.56
O (wt %)	1.08	1.03	0.69	1.01	0.8	0.66	0.83	0.77
S (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TAN (mg KOH/g)	0.018	0.000	0.000	0.000	0.743	0.063	0.180	0.000
Al (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	4.4	<5.5	<4.0
Ca (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	<4.0	<5.5	<4.0
K (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	<4.0	<5.5	<4.0
Mg (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	<4.0	<5.5	<4.0
Mn (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	<4.0	<5.5	<4.0
Na (ppm)	<5.5	<5.5	<4.0	<5.5	12.4	<4.0	<5.5	<4.0
P (ppm)	<5.5	<5.5	<4.0	<5.5	<5.5	<4.0	<5.5	<4.0
Si (ppm)	11.1	<5.5	<4.0	<5.5	6.0	26.0	<5.5	<4.0
S (ppm)	<5.5	<5.5	<4.0	<5.5	49.4	<4.0	<5.5	<4.0
Aqueous Phase								
C (wt %)	0.19	0.15	0.16	0.15	0.48	0.78	0.53	0.2
H (wt %)	11.92	11.65	10.98	11.88	10.71	10.77	11.41	11.56
S (wt %)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N (wt %)	0.06	0.04	0.09	0.01	0.42	0.94	0.27	0.08
Al (ppm)	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Ca (ppm)	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
K (ppm)	<2.0	<2.0	<2.0	<2.0	2.0	<2.0	<2.0	2.0
Mg (ppm)	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Mn (ppm)	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Na (ppm)	20	16	18	20	15	14	10	11
P (ppm)	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Si (ppm)	41	42	150	130	24	81	13	19
S (ppm)	9.4	43	59	88	180	570	140	65

the results are similar to that found in the literature. Herbaceous materials resulted in the lowest oil yields at 56.2 wt % for the corn stover and 62.1 wt % for the switchgrass. This compares to literature values of 58.2 wt % for corn stover²⁸ and 60.7 wt % for switchgrass.²⁹ These values are considered to be within acceptable experimental ranges considering the highly variable nature of these feedstocks. Also displayed in Table 3 are the inorganic contents of the pyrolysis oils, which were remarkably low for all of the feedstocks, probably because the vapors were filtered prior to condensation (see Figure 1). Also notable is that the sulfur contents of the oils from the herbaceous materials were substantially greater than those from the woody materials.

3.3. Upgraded Oil Yields and Characterization. As seen in Table 4, the upgraded oil yield varied significantly, ranging from 40 to 57% (g fuel/g dry feed). This range is moderately higher than the values reported by Elliott et al. when hydrotreating

a bio-oil derived from pine sawdust, where yields of 39–43% (g fuel/g dry feed) were observed.³⁰ The lowest value, observed from tulip poplar, corresponded to a low overall mass balance. This experiment was repeated, and the mass balance and yield improved. The tulip poplar was still the worst-performing feedstock in terms of conversion to fuel at 40.1%, while the corn stover performed best at 56.8%. Previous research by Elliott reported the yield for poplar at 21.2% (g oil/g dry feed);³¹ however, this result was from 1988, and the technology has seen numerous advances. The agricultural residue result fits in the ranges reported by Capunitan and Capareda, where batch hydrotreatment of corn stover resulted in yields ranging from 38 to 67%.³² The blended materials showed performance comparable to that of the clean and whole pine materials. The field-to-fuel yield was then calculated by multiplying the fast pyrolysis oil yield by the upgraded oil yield. This allows for an even comparison across feedstocks, given that some materials

may have a high fast pyrolysis oil yield but a low upgraded oil yield. As seen in Table 4, the field-to-fuel yield ranges from 17 to 27% on an organic matter basis and from 30 to 48% on a carbon throughput basis. The clean woody materials have the highest yields, while the grass and corn stover have the lowest yields. The blended feedstocks exhibit a field-to-fuel yield that is lower than that of the clean pine but approximately equal to that of the whole pine and poplars.

Characterization of the oil and aqueous phases from the hydro-treater, as seen in Table 5, indicates that there is little variation in the CHNO/S composition. In all cases, deoxygenation was nearly complete, with all oils exhibiting less than 1.1% O. The TAN values were negligible in most cases, although an elevated TAN level was observed in the switchgrass and in blend 1. Because blend 1 contains 33 wt % switchgrass, this suggests that the use of switchgrass and some herbaceous feedstocks may lead to upgraded oil that is more corrosive. Table 5 also shows the inorganic analysis of the oil and aqueous phases as determined by inductively coupled plasma–optical emission spectrometry. The oil phase showed very little inorganic content, with only Si and S present in more than a single sample. The Si most likely is carryover from the glass wool used to support the catalyst bed between reaction zones, and the S is likely carryover from the sulfided catalyst.³³ Aluminum was detected in the corn stover sample, although at a level barely above the quantifiable limit. Sodium was detected only in the switchgrass oil. The aqueous fractions contained significantly higher concentrations of inorganic material, although again the only compounds observed were Na, Si, and S.

Figure 3 graphically depicts the yields of the feedstocks for the fast pyrolysis, hydrotreating (upgrading), and combined fast

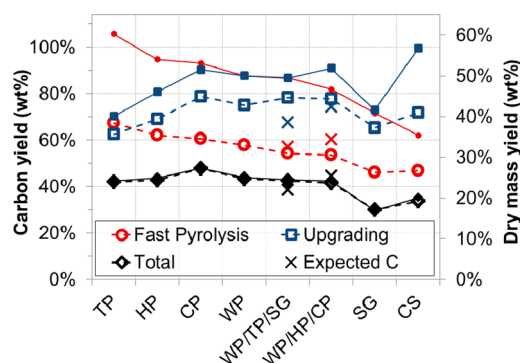


Figure 3. Yields of feedstocks for the fast pyrolysis, hydrotreating (upgrading), and combined fast pyrolysis and hydrotreating processes (total) as a ratio of total product carbon to total input carbon (hollow markers, left axis) and as a ratio of dry oil product to dry ash-free infeed material (solid markers, right axis). X's represent expected values on a carbon basis for the blends based on the sum of the constituents.

pyrolysis and hydrotreating (total) processes. Results shown as solid markers represent the ratio of dry oil product to dry ash-free infeed material, while hollow markers represent the ratio of total product C to total input C. Note that the right vertical axis (dry mass yield) has been scaled so that the total process yields align with those using a carbon basis (left vertical axis). Also, the feedstocks have been sorted in descending order of fast pyrolysis mass yield because this is the metric most commonly used to assess pyrolysis oil yield. Although integrated studies were not found in the literature, the techno-economic analysis performed by Jones et al.¹⁶ included an in-depth literature review that

Table 6. Gasoline, Diesel, Heavies, and Jet Fuel Fractions of the Upgraded Fuels by Simulated Distillation as Weight Percentages^a

feed	gasoline fraction	diesel fraction	heavies fraction	jet fraction
clean pine	39	44	17	12
whole pine	42	44	14	11
tulip poplar	40	46	14	12
hybrid poplar	45	42	13	11
switchgrass	47	42	11	11
corn stover	51	40	9	12
blend 1	44	43	13	11
blend 2	45	42	13	11

^aThe sum of the fractions is greater than 100% because of the overlap of the jet and diesel boiling point ranges.

produced a “best case” scenario. In this scenario, the pyrolysis oil yield of a clean, low ash feedstock was set at 64% (g dry oil/g dry biomass) and the upgrading yield was set at 44% (g upgraded oil/g dry bio-oil). This results in a total yield of 28.2%, which compares to the highest yield in this study of 27.4%. Although upgrading yields from this study were generally higher than the 44% value used in the analysis, as seen in Table 4, fast pyrolysis conversion performance yields were lower. Given that the work of Jones et al. was a “best case” scenario, the agreement between their numbers and the highest yield from this study suggest that the yield values obtained are realistic.

It is apparent that the yields of the feedstocks are very different in the fast pyrolysis and upgrading processes and that the efficiencies of both processes must be considered to understand the total conversion of the feedstocks to fuel, even on a qualitative basis. In particular, the relative yield performance of the hybrid poplar, tulip poplar, and switchgrass in the different processes depends upon whether the metric is total dry product yield or C yield. As expected, C yields are higher than mass yields. Another important point is that the total process C yields of the woody materials and blends are 42–43%, except for clean pine, which had a C yield of 48%. Both blends exhibited fast pyrolysis yields that were lower than expected from the sum of their constituents on a mass or C basis but upgrading yields that were higher than expected.

Expected values for the blends are shown as X's in Figure 3. Overall, blend 1 exhibited a total process C yield that was 4% higher than expected, while blend 2 exhibited a total process C yield that was 3% lower than expected. A final consideration in comparing the conversion performance of the different materials is that all materials were subjected to fast pyrolysis at a reactor temperature of 500 °C. Previous tests indicate that this temperature optimizes the liquid bio-oil yield from pine materials; however, other materials may have higher yields at higher or lower reactor temperatures, so the yield results presented in Figure 3 are not necessarily optimized for all feedstocks. For example, higher yields have been observed for switchgrass using lower fast pyrolysis temperatures of 480 °C rather than 500 °C.³⁴ Interestingly, these results indicate that blending may reduce the impact of operating conditions on specific components in blends because the performance of blend 1 in fast pyrolysis was higher than expected. These results also indicate that the effects of minerals in the feedstock do not linearly affect total process yields. For example, the mineral contents of the tulip poplar,

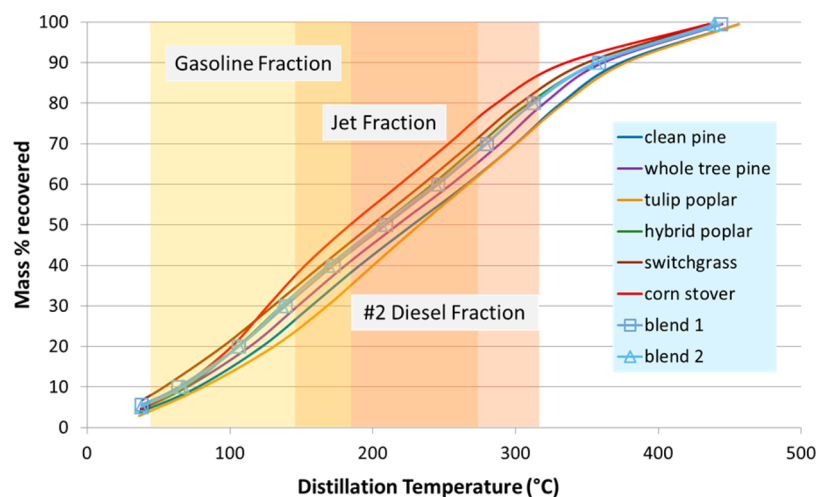


Figure 4. Simulated distillation results of the upgraded oils.

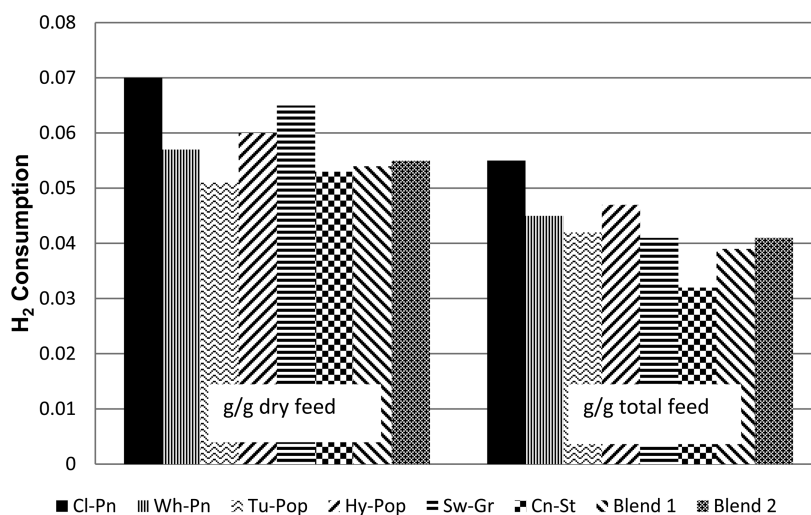


Figure 5. Hydrogen consumption of the fast pyrolysis bio-oils during the hydrotreatment process.

hybrid poplar, whole-tree pine, and blends were all quite different, yet their total process yields were similar. The fact that the clean pine exhibited a total process yield better than that of any of the other materials indicates that small perturbations in properties may have profound implications in conversion performance. For example, other research has shown that small amounts of alkali and alkaline earth metals significantly affect fast pyrolysis; however, the effects on conversion are nonlinear, and as the concentration of inorganics increases, the impact becomes relatively weaker. Because replications were not performed in this preliminary study, additional tests are needed to establish the significance of these findings.

As seen in Table 6, the simulated distillation of the final upgraded fuel highlights variations in the fuel quality as a function of feedstock. The data are shown graphically in Figure 4. Little variation was observed between the jet fuel fractions, with all oils exhibiting 11–12%. The gasoline fraction showed considerably more spread, ranging from 39 to 51%. The two oils with the greatest gasoline fraction were the corn stover and switchgrass, while the lowest fraction was found in the clean pine. The diesel fuel content was more constant, ranging from 40% in the corn stover to 46% in the tulip poplar. The heaviest fraction also exhibited a wide range, with the lowest fraction seen in the corn stover, while the highest was observed in the clean pine. These

values are consistent with the simulated distillation ranges reported by Elliott when analyzing a number of different hydrotreated oils.³⁵ The data indicate that, in addition to overall yield, the biomass feedstock used affects the ultimate composition of the final fuel.

One of the factors that will play a role in the economic feasibility of large-scale hydrotreatment is the amount of H_2 required by the reaction. As seen in Figure 5, the amount of H_2 consumed during the upgrading process can vary widely across feedstocks. Clean pine requires the most H_2 on a dry feed basis, while tulip poplar requires the least H_2 . Of particular interest are the blends, which require less H_2 than any of the woody feedstocks with the exception of the tulip poplar. On an “as-received” basis, the blends required the least H_2 of any feedstock except corn stover. These results illustrate three possible advantages of blends over single-material feedstock materials. First, blends may have conversion performance higher than that of the sum of their constituents because of nonlinear conversion, i.e., chemical interactions related to composition may result in conversion performance that is not accurately predicted by simply summing the weighted fractions of the pure components. Second, blends may consume less H_2 than would be expected based on the sum of their constituents. Third, because of the economics of supply and demand, large quantities of blended

feedstocks will likely be available for lower costs than single-feedstock materials.

All of the data gathered from the various aspects of this study and presented in this paper were used to build multivariate models to predict the yields of the pyrolysis and upgrading steps. However, there was insufficient data to validate the model predictions. Future work will include testing additional samples to validate the models developed.

4. CONCLUSIONS

This study has shown that the compositional parameters of the biomass feedstock will affect both the bio-oil generated by fast pyrolysis as well as the final quantity and quality of the upgraded fuel blendstock. Although some feedstocks, such as tulip poplar, generate a high yield of bio-oil, the bio-oil does not necessarily exhibit a high yield in the hydrotreater; therefore, the product yields and qualities of both fast pyrolysis and hydrotreating must be considered in comparing the conversion performance of different biofuel feedstock materials, including blends. Another important consideration is that nonlinearities in conversion and upgrading processes may cause blended materials to perform better or worse than separated feed streams. Specifically, results obtained from clean pine, whole-tree pine, and other samples in this work indicate that the effects of small changes in key properties, such as mineral content, may have profound effects on conversion performance. However, larger changes in key properties do not have correspondingly larger effects on conversion, indicating that the relationship between feedstock attributes and conversion properties is nonlinear. These results also demonstrate that the product distributions of upgraded fuels can vary widely depending on the feedstock.

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Notes

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■ REFERENCES

- (1) DOE. *Bioenergy Technologies Office Multi-Year Program Plan*; Department of Energy: Washington, DC, 2013.
- (2) IPCC. *Climate Change 2007: Synthesis Report section 2.4, Attribution of Climate Change*; Intergovernmental Panel on Climate Change (IPCC), 2007.
- (3) Watkins, E. Watching the World: Iran Woos Latin America. *Oil Gas J.*, Jan 16, 2012.
- (4) Jimenez-Rodriguez, R.; Sanchez, M. Oil Price Shocks and Real GDP Growth: Empirical Evidence for Some OECD Countries. *Appl. Econ.* **2005**, *37* (2), 201–228.
- (5) EIA. *August 2014 Monthly Energy Review*; Department of Energy - U.S. Energy Information Administration: Washington, DC, 2014.
- (6) Di Blasi, C.; Signorelli, G.; Di Russo, C.; Rea, G. Product distribution from pyrolysis of wood and agricultural residues. *Ind. Eng. Chem. Res.* **1999**, *38* (6), 2216–2224.
- (7) Di Blasi, C.; Branca, C.; Santoro, A.; Gonzalez Hernandez, E. Pyrolytic behavior and products of some wood varieties. *Combust. Flame* **2001**, *124* (1), 165–177.

- (8) Agblevor, F.; Besler, S.; Wiseloge, A. Production of oxygenated fuels from biomass: Impact of feedstock storage. *Fuel Sci. Technol. Int.* **1996**, *14* (4), 589–612.

- (9) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* **2009**, *24* (2), 1380–1388.

- (10) 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* (2), 491–515.

- (11) Grange, P.; Laurent, E.; Maggi, R.; Centeno, A.; Delmon, B. Hydrotreatment of pyrolysis oils from biomass: Reactivity of the various categories of oxygenated compounds and preliminary techno-economic study. *Catal. Today* **1996**, *29* (1), 297–301.

- (12) Bridgwater, A. Principles and practice of biomass fast pyrolysis processes for liquids. *J. Anal. Appl. Pyrolysis* **1999**, *51* (1), 3–22.

- (13) Garcia-Perez, M.; Wang, X. S.; Shen, J.; Rhodes, M. J.; Tian, F.; Lee, W.-J.; Wu, H.; Li, C.-Z. Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products. *Ind. Eng. Chem. Res.* **2008**, *47* (6), 1846–1854.

- (14) Bryden, K.; Weatherbee, G.; Habib, E. Flexible pilot plant technology for evaluation of unconventional feedstocks and processes. *Catalagrum* **2013**, *113*, 3–21.

- (15) 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.

- (16) Jones, S.; Meyer, P.; Snowden-Swan, L.; Padmaperuma, A.; Tan, E.; Dutta, A.; Jacobson, J.; Cafferty, K. *Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: Fast pyrolysis and hydrotreating bio-oil pathway*; National Renewable Energy Laboratory (NREL): Golden, CO, 2013.

- (17) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erblich, D. C. *Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply*; DTIC Document, 2005.

- (18) Perlack, R. D.; Eaton, L. M.; Turhollow, A. F.; Langholtz, M. H.; Brandt, C. C.; Downing, M. E.; Graham, R. L.; Wright, L. L.; Kavkewitz, J. M.; Shamey, A. M. *US billion-ton update: Biomass supply for a bioenergy and bioproducts industry*; ORNL/TM-2011/224; Oak Ridge National Laboratory: Oak Ridge, TN, 2011.

- (19) Fahmi, R.; Bridgwater, A. V.; Donnison, I.; Yates, N.; Jones, J. M. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* **2008**, *87* (7), 1230–1240.

- (20) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids. *Energy Fuels* **2003**, *17* (1), 1–12.

- (21) Carrier, M.; Joubert, J.-E.; Danje, S.; Hugo, T.; Görgens, J.; Knoetze, J. Impact of the lignocellulosic material on fast pyrolysis yields and product quality. *Bioresour. Technol.* **2013**, *150* (0), 129–138.

- (22) Zhang, Q.; Chang, J.; Wang, T.; Xu, Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers. Manage.* **2007**, *48* (1), 87–92.

- (23) INL. *The Feedstock Logistics Design Case for Multiple Conversion Pathways*; Idaho National Laboratory Bioenergy Program, 2014.

- (24) NREL. *Summative Mass Closure*; NREL/TP-510-48087; National Renewable Energy Laboratory: Golden, CO, 2011.

- (25) Evans, R. J.; Milne, T. A. Molecular characterization of the pyrolysis of biomass. *Energy Fuels* **1987**, *1* (2), 123–137.

- (26) Sykes, R.; Kodrzycki, B.; Tuskan, G.; Foutz, K.; Davis, M. Within tree variability of lignin composition in Populus. *Wood Sci. Technol.* **2008**, *42* (8), 649–661.

- (27) Kim, K. H.; Eom, I. Y.; Lee, S. M.; Choi, D.; Yeo, H.; Choi, I.-G.; Choi, J. W. Investigation of physicochemical properties of biooils produced from yellow poplar wood (*Liriodendron tulipifera*) at various temperatures and residence times. *J. Anal. Appl. Pyrolysis* **2011**, *92* (1), 2–9.

- (28) Mullen, C. A.; Boateng, A. A.; Goldberg, N. M.; Lima, I. M.; Laird, D. A.; Hicks, K. B. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass and bioenergy* **2010**, *34* (1), 67–74.

(29) Boateng, A. A.; Daugaard, D. E.; Goldberg, N. M.; Hicks, K. B. Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-Oil Production. *Ind. Eng. Chem. Res.* **2007**, *46* (7), 1891–1897.

(30) 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* (6), 3891–3896.

(31) Elliott, D. C. *Upgrading of Fast Pyrolysis Bio-oil*. Presented at Aalto University, 2014.

(32) Capunitan, J. A.; Capareda, S. C. Hydrotreatment of corn stover bio-oil using noble metal catalysts. *Fuel Process. Technol.* **2014**, *125*, 190–199.

(33) Panisko, E.; Wietsma, T.; Lemmon, T.; Albrecht, K.; Howe, D. Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks. *Biomass Bioenergy* **2015**, *74*, 162–171.

(34) Mullaney, H.; Farag, I.; LaClaire, C.; Barrett, C. *Technical, Environmental and Economic Feasibility of Bio-Oil in New Hampshire's North Country*; 14B316 UDKEIF, ABAN-URI-BO43; University of New Hampshire: Durham, NH, 2002

(35) Elliott, D. C. Historical Developments in Hydroprocessing Bio-oils. *Energy Fuels* **2007**, *21* (3), 1792–1815.