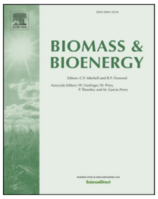
Biomass and Bioenergy 96 (2017) 142–151

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe



Research paper

Catalytic hydroprocessing of fast pyrolysis oils: Impact of biomass feedstock on process efficiency

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ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form
8 September 2016
Accepted 12 September 2016
Available online 1 December 2016

Keywords:
Biofuels
Fast pyrolysis
Catalytic hydrodeoxygenation
Hydrotreating

ABSTRACT

We report here on an experimental study to produce refinery-ready fuel blendstocks via catalytic hydrodeoxygenation (upgrading) of pyrolysis oil using several biomass feedstocks and various blends. Blends were tested along with the pure materials to determine the effect of blending on product yields and qualities. Within experimental error, oil yields from fast pyrolysis and upgrading are shown to be linear functions of the blend components. Switchgrass exhibited lower fast pyrolysis and upgrading yields than the woody samples, which included clean pine, oriented strand board (OSB), and a mix of piñon and juniper (PJ). The notable exception was PJ, for which the poor upgrading yield of 18% was likely associated with the very high viscosity of the PJ fast pyrolysis oil (947 cp). The highest fast pyrolysis yield (54% dry basis) was obtained from clean pine, while the highest upgrading yield (50%) was obtained from a blend of 80% clean pine and 20% OSB (CP_8OSB_2). For switchgrass, reducing the fast pyrolysis temperature to 450 °C resulted in a significant increase to the pyrolysis oil yield and reduced hydrogen consumption during hydrotreating, but did not directly affect the hydrotreating oil yield. The water content of fast pyrolysis oils was also observed to increase linearly with the summed content of potassium and sodium, ranging from 21% for clean pine to 37% for switchgrass. Multiple linear regression models demonstrate that fast pyrolysis is strongly dependent upon the contents of lignin and volatile matter as well as the sum of potassium and sodium.

1. Introduction

The production of renewable motor fuels from lignocellulosic biomass is an attractive alternative to petroleum-based fuels, and remains a key part of the U.S. strategy to ease dependence on imported oil and reduce greenhouse gas emissions [1]. However, for this strategy to be both environmentally and economically feasible, it is important that the development of conversion technologies and biomass resources be coordinated so that the cost-competitive production of biofuels is compatible with the use of sustainable, low-cost, and diverse feedstocks [2,3]. The 2016 Billion Ton Update provides a comprehensive survey of U.S. biomass resource potential, including price and supply curves for various biomass types [4]. While this report affirms the annual availability of a billion tons of biomass that could potentially be converted to motor fuel, the question of feedstock quality is not specifically addressed. To complement the 2016 Billion Ton Update there is a considerable need to understand how different biomass types perform in different conversion processes, including impacts to operations, process efficiency, product quality, and potential waste streams.

One potential thermochemical route to convert biomass to motor fuels is via fast pyrolysis, using rapid heating to moderate temperatures (roughly 500 °C), without oxygen, to convert biomass into solid (char), gas, and liquid (bio-oil) products. The liquids contain upwards of 75% of the starting biomass energy content, but have several undesirable properties that limit their direct use downstream, including instability, low heating value, high viscosity, and high acidity [5]. These properties generally result from a high proportion of oxygenated compounds of varying chemical functionality that need to be removed from the oil. The most common method employed is catalytic hydrodeoxygenation at elevated pressures [6], which generates a hydrocarbon liquid

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http://dx.doi.org/10.1016/j.biombioe.2016.09.012

suitable for co-processing in a petroleum refinery or blending into finished fuel [7]. The literature contains numerous studies that have investigated the pyrolysis behavior of various feedstocks [8], and some have examined the effect of bio-oil characteristics on hydrotreating [9,10]. While much progress has been made in recent years, there are still large gaps to close in making this route to biofuels cost-competitive. These are primarily due to the complex chemical and physical nature of the oil, which eludes comprehensive characterization, and the closely-related development of robust hydrotreating catalysts, as pointed out by Wang et al. [11]. Fahmi et al. have reported that as the lignin content in the feedstock increases, the organic liquid yield from fast pyrolysis also increases [12]. Other studies have shown an inverse relationship between the ash content and bio-oil yields [13–15]. In addition to product yields, the amount and speciation of inorganic compounds present in the feedstock can affect the bio-oil composition, as higher mineral content leads to higher levels of low molecular weight compounds such as formic acid, glycoaldehyde, and acetol, while decreasing anhydro-sugars like levoglucosan [16]. The pyrolysis step, however, is only one unit operation in the process to produce finished fuel blendstocks, as the bio-oil still must be upgraded via hydrotreatment. Many of the bio-oil contaminants that result in lower hydrotreater yields can be traced back to the feedstock, such as residual solids (char), alkali metals, and high water content in the bio-oil [17]. Hence, in order to fully understand the effect feedstocks have on the yield and quality of finished fuel blendstocks, the integrated pathway must be studied rather than individual unit operations. A recent study by Zacher et al. examined the performance of pine beetle-killed trees and “hog fuel” (mix of woody residues) providing important data for two low-cost resources [18]. Still, as the vast majority of past work has focused on processing clean woody materials, it is difficult to assess, based on the literature, how or why feedstock type or, more specifically, the pyrolysis oil derived from it, affects the outcome of the hydrotreating process.

The impact of feedstock characteristics on thermochemical processing to advanced hydrocarbon biofuels has become a focal point of both academic and U.S. Department of Energy research efforts. Key to the research efforts underway is the ability to simultaneously achieve DOE's feedstock cost, quality, and volume targets, while also achieving conversion cost targets that have been established as benchmarks needed for biofuels to be competitive with petroleum fuels. To this end, Idaho National Laboratory (INL), Pacific National Laboratory (PNNL), and the National Renewable Energy Laboratory (NREL) are partnering to understand the field-to-fuel implications of using different feedstocks in thermal conversion processes. Recently, we reported results from an integrated fast pyrolysis-hydrotreating study for several commercially-relevant feedstocks [19]. This work showed that feedstock choice indeed impacted multiple conversion metrics, including bio-oil yield and composition, hydrotreating yield, H_2 consumption, selectivity to fuel products, and biomass carbon-to-fuel efficiency. Follow-on projections from technoeconomic analyses confirmed that overall conversion costs vary significantly with feedstock, indicating an approximate 40% increase in the cost to convert switchgrass to fuel compared to the base case of clean pine [20]. We report here on these and additional conversion tests and analyses that relate fast pyrolysis and hydrotreating performance to physical and bulk chemical properties of the inputs for each process step, i.e. raw feedstock and pyrolysis oil. The overall processing efficiency as a function of feedstock was examined on the basis of mass, carbon, and chemical energy of the inputs and products.

2. Materials and methods

2.1. Feedstock selection and characterization

The feedstocks for these experiments, shown in Table 1, were acquired and prepared by INL and were chosen to represent significant resources identified in the Billion Ton Update [4]. Feedstocks were included that are available in sufficient quantity to be impactful (~50 million tons/year combined) and that could potentially be blended to meet DOE's cost target for delivered material of $80/dry ton. Oriented strand board (OSB) was chosen to represent the wood-based fraction of construction and demolition waste. Von Holle et al. has reported that piñon-juniper has an unusually high carbon conversion yield of nearly 35% in catalytic fast pyrolysis and that the resulting crude oil had a low oxygen content of approximately 11% [21]. A similar piñon-juniper was included in the present study for comparison. All feedstocks were ground to less than 2 mm. Feedstock characterization included compositional, proximate, ultimate, and elemental ash analyses as described previously [19]. Details of the analytical methods used can be found in the Supplemental Information.

2.2. Fast pyrolysis processing and product characterization

Pyrolysis oils were produced using a 5 cm (2 in.) fluidized bed reactor system (2FBR), which has been described previously [19]. A schematic can be found in the Supplemental Information (see Figure S-1). Briefly, biomass was fed at a rate of 420 g/h by an auger into the 2FBR, which was operated at 500 °C, with the goal of generating 1 L of pyrolysis oil from each feedstock. Char exiting the 2FBR was removed by a cyclone and remaining fines were removed using a hot, in-line vapor filter (2 μm pleated, 316-SS screen). The process lines, cyclone, and filter were heat traced and maintained at approximately 400 °C. The residence time of pyrolysis vapors in the 2FBR system before the condensation train was approximately 2 s. Vapors were condensed in a three-stage condensation train; an air-cooled condenser, followed by an electrostatic precipitator and a dry ice condenser. The total volume of non-condensable gases was measured with a dry test meter before being analyzed by NDIR, GC, and TCD to measure H_2, CH_4, CO, CO_2, and C_2/C_3 hydrocarbons.

A number of techniques were used to analyze the liquid and solid products from the 2FBR. The pyrolysis oils and chars were characterized using proximate, ultimate, and elemental ash analysis. Additional measurements performed on the oils included water content, viscosity, density, acid content, carbonyl content, and calorimetry. Except for carbonyl content, detailed descriptions of the analytical methods have been described previously [19] and are summarized in the Supplemental Information. Carbonyl content was determined by automated titration based on a method originally proposed by Faix [22]. Approximately 0.1 g of oil was dissolved in DSMO (dimethyl sulfoxide) and reacted with a standard mixture of hydroxyl amine hydrochloride:TEA (triethanol amine) for 2 h at 80 °C. The reaction of carbonyl groups in the oil consumed some of the hydroxyl amine and the TEA reacted with the liberated hydrogen chloride. The excess TEA was then back-titrated with standardized hydrochloric acid. Each oil sample was prepared and analyzed in triplicate.

2.3. Pyrolysis oil hydroprocessing and product characterization

The whole pyrolysis oils produced in the 2FBR were upgraded using a two-stage hydrotreater to produce a refinery-ready fuel. A detailed description of the hydrotreating system is given elsewhere [19] and a process flow diagram can be found in the Supplemental Information (Figure S-2). Briefly, the whole oils were introduced by

Table 1
Key properties of raw biomass feedstocks as determined by compositional, proximate, ultimate, and elemental ash analyses.

Feedstock	Clean pine	Switch-grass	OSB	Piñon-juniper	Blend	Blend	Blend	Blend
Origin	Butler, AL	Garvin, OK	Bonneville, ID	Beaver, UT	various	various	various	various
Designation	CP	SG	OSB	PJ	$CP_1TP_1\ SG_1$	CP_8OSB_2	$CP_7OSB_2\ SG_1$	$CP_4OSB_2\ SG_4$
Moisture (wt-%)	3.50	6.66	2.39	9.75	4.19	3.76	4.08	4.66
(Dry basis)								
Ash (wt-% dry)	0.71	4.32	1.14	3.69	1.97	0.80	1.16	2.22
K + Na (ppm)	809	6600	2209	3393	2820	1089	1619	3207
Ash closure (%)	95.6	98.2	85.1	98.7	99.2	93.2	93.5	94.4
(wt-% dry, ash-free)								
Volatile matter	84.6	83.8	84.9	83.7	84.6	85.4	85.3	84.7
HHV (MJ/kg)	21.2	20.2	20.9	21.6	20.4	20.6	20.6	20.4
LHV (MJ/kg)	18.1	17.0	17.7	18.0	17.1	17.5	17.4	17.3
C	51.4	50.8	50.7	55.1	50.4	50.8	50.8	50.6
H_2O extractives	1.5	5.1	2.7	7.2	2.6	1.7	2.2	3.4
EtOH extractives	2.8	2.5	2.9	7.0	1.9	2.8	2.7	2.6
Glucan	38	34	42	27	40	39	39	37
Xylan	6.9	22.3	14.3	7.6	13.9	8.4	9.7	13.8
Lignin	28.8	17.8	22.2	27.9	24.1	27.6	26.4	23.8
Mass closure[a]	96.9	97.7	98.7	94.7	94.7	94.7	96.3	96.2

Clean pine is debarked and de-limbed whole trees. OSB is oriented strand board. TP in blend is tulip poplar.

[a] Mass closure refers to mass closure of compositional analysis as detailed in Table S-2.

syringe pump into the reactor along with He and H_2 in stoichiometric excess. The reactor had an inner diameter of 1.3 cm and an overall length of 63.5 cm and was operated at 10.7 MPa (1550 psi). The first zone contained a Ru/C catalyst and was operated at 220 °C, while the second zone utilized a Co/Mo catalyst on an alumina support and was operated at 400 °C. The liquid products were collected in a pressurized sample reservoir that was drained every 12 h, and the oil and aqueous phases were subsequently gravity separated. The gases exiting the reactor were measured by a Dry-Cal flow meter and analyzed by GC.

The liquid product from hydrotreating was distinctly two-phase and easily separated for weighing and analysis. The oil phase from the steady-state portion of each test, defined by a constant observed density of the product oil, was combined to give enough sample for analysis. This composite was analyzed for water content, density, viscosity, C/H/N/S, acid number, and elemental ash. Due to the high carbon content of the oil, acetanilide, at 71.1% C, was used for instrument calibration for C content, along with subsequent checks using fuel oil standards at 85–86% C. Simulated distillation was also carried out on the oil fractions to determine the mass fractions boiling in the gasoline, diesel, and jet fuel ranges. Details of the analytical methods used can be found in Howe et al. [19], and are also summarized in the Supplemental Information.

3. Results and discussion

3.1. Feedstock characterization

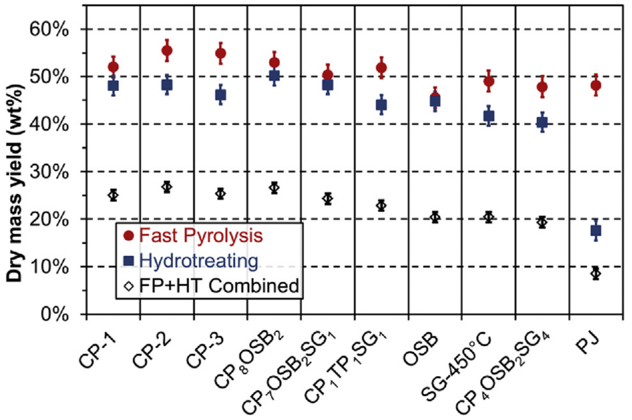

Fig. 1. Yields from fast pyrolysis (FP), hydrotreating (HT), and combined fast pyrolysis and hydrotreating (FP + HT) processes for several biomass feedstocks as a ratio of dry oil product to dry, ash-free infeed material.

The complete raw feedstock properties as measured by fuel analysis (proximate, ultimate, calorific) and compositional analysis (carbohydrates, lignin, extractives, protein) are shown in Table S-1. As expected, the switchgrass and its blends contain more ash, higher moisture, and less lignin than the woody feedstocks. The piñon-juniper was also significantly higher in moisture, ash, and extractives, and significantly lower in sugars compared to the other feedstocks. It also contained more than 1.2 wt-% calcium, which is 3–11 times more than the other native feedstocks. The OSB, an engineered wood product, also contained more Ca and Na than most feedstocks. We expect this is due to the manufacturing process, which is reported to use various resins and borate compounds. Key differences in the individual feedstock properties, especially properties that appear to be influential in determining conversion performance, are summarized in Table 1.

3.2. Conversion performance

3.2.1. Fast pyrolysis results

Fig. 1 summarizes the yields of the pure feedstocks and blends for the fast pyrolysis (FP), hydrotreating (HT) and combined fast pyrolysis and hydrotreating (FP + HT) processes as a ratio of dry oil product to dry infeed material. For comparison, Supplementary Figure S-4 shows the same data, but also includes results (marked by *) that were obtained using similar conversion reaction conditions as previously reported by Howe et al. [19]. Importantly, the sample designated CP*-2 was mistakenly identified as whole pine (Wh-Pn) in Howe et al. Characterization tests have shown that CP*-2 has similar organic and inorganic chemical composition as CP*-1, and it was obtained from the same location at the same time as sample CP*-1 [23]; consequently, in this work it is considered a replicate of the clean pine (CP), providing a total of five replicate tests of that material. The uncertainty bars shown in Fig. 1 are estimated from the five replicates of clean pine and are 2.3, 3.6 and 2.0 wt% for FP, HT and FP + HT, respectively.

Detailed fast pyrolysis product distributions and key

Table 2
Fast pyrolysis product distributions and key analyses.

	CP	SG_{500} [19]	SG_{450}	OSB	PJ	CP_1TP_1 SG_1	CP_8OSB_2	CP_7OSB_2 SG_1	CP_4OSB_2 SG_4
Fast Pyrolysis Product Yields (wt-% of biomass feed)									
Total liquid	65.0 ± 1.6	58.1	62.5	59.1	57.9	63.7	64.5	62.7	60.6
Char	12.5 ± 0.8	10.8	18.2	14.3	15.3	13.0	12.8	13.5	14.8
Gas	16.6 ± 1.0	18.1	13.9	20.3	17.5	17.0	17.5	17.4	17.8
Mass balance	94.1 ± 0.9	87.0	94.6	93.7	90.7	93.7	94.6	94.2	93.6
Fast Pyrolysis Liquid Analysis (wt-% as received unless otherwise noted)									
Ash (wt-%, dry)	0.4 ± 0.2^{+}	–	0.2	0.7	0.3	0.4	0.2	0.4	0.3
C	45.8 ± 0.8	35.1	40.0	44.0	50.3	43.9	45.3	45.4	42.5
H	7.7 ± 0.3	9.0	7.9	7.8	8.6	7.6	7.6	7.6	7.9
N	0.07 ± 0.01	0.36	0.43	0.47	0.49	0.19	0.13	0.16	0.30
O	46.2 ± 0.8	55.4	51.6	47.1	40.4	48.0	46.8	46.5	49.0
S (ppm)	46 ± 7	240	374	51	278	96	78	56	174
H_2O (wt-%)	21.2 ± 0.9	37.0	29.8	25.6	27.6	23.6	21.6	23.9	26.4
TAN	49.6 ± 10.2	104.3	101.4	76.3	61.5	74.1	65.8	62.8	71.7
Carbonyl	5.5 ± 0.1^{+}	–	4.60	3.91	2.88	4.88	4.92	4.53	4.48
Viscosity	49.1 ± 5.4^{+}	–	20.9	39.1	947.0	34.1	42.5	50.1	29.8
Density	1.19 ± 0.01^{+}	–	1.18	1.12	1.08	1.17	1.21	1.21	1.23
HHV (MJ/kg)	26.6	24.3	23.3	26.4	36.8	–	24.1	24.2	24.3
LHV (MJ/kg)	21.3	16.4	16.9	20.4	30.3	–	18.7	18.6	18.2
% feed C→oil	63.1 ± 0.5	46.2	56.7	53.1	62.3	59.7	61.1	60.1	55.5

Average values and standard deviations for CP are from the five replicates; SG_{500} char yield low due to collection system malfunction; units are TAN (mg/g KOH), Carbonyl (mol/kg), Viscosity (cp, 40 °C, SG_{500} at 25 °C), Density (g/cm3, 20 °C).

characterization data are shown in Table 2, where the CP data are shown as averages and standard deviations of the five pine replicates. Complete fast pyrolysis product characterization from the current work can be found in Table S-2. The ash, carbonyl, and density values of the pyrolysis oil from the previously published experiments were not available, and the viscosity was measured at a different temperature. Hence, the CP values for these measurements, noted by '+' in the table, are the average of the most recent three replicates. Replicate tests of blended materials indicate that the experimental uncertainties are similar for all feedstocks as described further below.

For the current tests, fast pyrolysis oil yields on a dry, ash-free basis ranged from 46% for OSB to 53% for the pine (average); char yields ranged from 13% for the CP_8OSB_2 to 18% for SG_{450}; gas yields were tightly grouped near 18%, except for OSB, which yielded 20%. The fraction of biomass carbon retained in the pyrolysis liquids ("% feed C→oil") ranged from 46% for switchgrass processed at 500 °C to 63% for clean pine (average). Notably, the carbon retained in the switchgrass oil increased by over 10% with a reduction in pyrolysis temperature. All of the oils contained less than 0.7 wt% ash. The low ash content is expected since, prior to condensation, the char is removed from the hot pyrolysis vapors by a cyclone separator followed by an inline 2 μm mesh screen filter. Elemental analyses of ash in the oil can be found in Table S-2, but the elements in the oil generally track the levels in the starting biomass, and included small amounts of Na, Mg, S, and Ca. A preliminary mass balance was conducted for these elements. On average, only a few percent of the magnesium and calcium from the starting biomass was contained in the oil, while approximately 15% of the sodium and nearly 50% of the sulfur was partitioned to the oil. Sulfur is present in biomass in several forms (organic sulfur in proteins, sulfate as counter ions) and is expected to be carried along as both organically-bound sulfur and hydrogen sulfide gasses. The inorganic sulfur likely remained in the char as the pyrolysis temperature was below the reduction temperature of sulfate in a reducing environment [24].

The water content of the fast pyrolysis oils ranged from 20.9% (CP) to 29.8% (SG). Alkali in biomass is known to catalyze the dehydration of biopolymers and increase reaction water yield;

Table 3
Hydrotreating product distributions and key product characterizations. The water content of the feed pyrolysis oil (as measured by KF) was mathematically subtracted and results are reported on a bone dry oil feed basis.

	CP	SG_{500} [19]	SG_{450}	OSB	PJ	CP_1TP_1 SG_1	CP_8OSB_2	CP_7OSB_2 SG_1	CP_4OSB_2 SG_4
Hydrotreating product yields (wt-% of dry pyrolysis oil feed)									
Fuel oil	48.8 ± 2.0	41.6	41.7	44.8	17.6	44.1	50.2	48.3	40.4
Water	35.4 ± 0.7	34.5	36.3	36.9	61.3	37.0	38.3	36.3	39.5
Gas	16.1 ± 1.5	21.0	22.0	18.3	17.8	18.9	11.5	15.4	20.1
Hydrotreating product analysis (oil phase only)									
C (wt-%)	87.7 ± 0.4	87.3	87.5	87.5	86.9	88.0	88.2	88.0	88.0
H (wt-%)	12.6 ± 0.2	12.9	12.1	13.2	14.0	13.0	12.6	12.3	12.8
O (wt-%)	1.08 ± 0.1	0.8	1.3	1.2	1.1	1.4	1.1	1.1	1.3
Gasoline	41 ± 2	47	42	46	61	36	41	40	42
Kerosene	30 ± 1	30	29	29	37	31	29	29	30
Diesel	45 ± 2	42	43	41	37	46	43	43	44
Heavies	14 ± 3	11	15	13	2	18	16	17	14
H_2 consumed	0.055 ± 0.011	0.065	0.047	0.048	0.063	0.047	0.051	0.059	0.045
HHV (MJ/kg)	44.0 ± 1.4	43.7	44.0	44.3	44.8	44.0	44.1	44.2	43.9
% oil C→fuel	73.7 ± 3.6	65.2	64.0	66.3	22.0	67.5	76.6	71.2	61.6

Boiling ranges are gasoline: 0–187 °C, kerosene: 160–266 °C, diesel: 187–345 °C, heavies: >345 °C; Units of H_2 consumption are g/g dry oil feed.

consequently, water content of the oils is plotted as a function of K + Na content in Supplemental Figure S-5, which shows that moisture content scales approximately with the content of K + Na. Notably, the measured water content of the pyrolysis oil from CP_2HP_1* (clean pine/hybrid poplar blend from Howe et al.) was substantially higher than the water contents of the oils from the CP replicates and HP. As further substantiated below, the measurement of water content in the CP_2HP_1* oil may be in error, and a proposed adjustment is shown in Supplemental Figure S-5. Other results of note from Table 2 were a higher than average acid content in the SG oil and a significantly higher viscosity observed for the PJ oil. At 947 cP, this value was more than 20 times the average for the other oils.

3.2.2. Hydrotreating results

Detailed hydrotreating product distributions and key characterization data are shown in Table 3, where the CP data are shown as averages and standard deviations of the five pine replicates. The complete fuel oil production and characterization results are presented in Table S-4. As shown in Fig. 1 and noted previously [19], the conversion yields of the feedstocks are quite different in the fast pyrolysis (FP) and hydrotreating (HT) processes. Notably, the OSB exhibited significantly poorer fast pyrolysis mass yields than the CP, while the hydrotreating yield was similar. For switchgrass, reducing the fast pyrolysis temperature to 450 °C resulted in a significant increase to the pyrolysis oil yield but did not directly affect the hydrotreating oil yield, although it did reduce the hydrogen consumption during hydrotreating. The fuel oil yields from the hydrotreater showed significant differences between feedstocks, ranging from 18% (PJ) to 50% (CP_8OSB_2). Yields for the other feedstocks were between 40 and 48%, while water produced ranged from 35 to 40% (except for PJ as discussed below), and gas was 12% (CP_8OSB_2) to 22% (SG_{450}), calculated by difference. The extremely low yield from the piñon-juniper oil may have been due to a phase separation occurring during the pumping process. The carbon and oxygen contents of the PJ pyrolysis oil were the highest and lowest, respectively, of all the feedstocks tested. This is usually indicative of a higher quality oil, in agreement with the result reported by Von Holle [21]. The low hydrotreating yield reported here was likely associated with the unusually high viscosity of the PJ pyrolysis oil (>900 cP compared to 40–50 cP for the other pyrolysis oils). The upgraded PJ oil exhibited the lowest viscosity and density of any of the blendstocks generated, suggesting that the “heavy” portion of the piñon-juniper bio-oil partially separated from the lighter fraction. Consequently, it is likely that only the light fraction, containing more water and fewer organics, was processed in the hydrotreater, resulting in a lower fuel oil yield and higher water yield. Indeed, the water yield for the PJ was 61%, compared to 35–40% for all other feedstocks.

Analysis of the oil phase showed that the elemental composition of the fuel blendstock was fairly consistent, with C concentrations ranging from 87 to 88 wt% and H concentrations ranging from 12 to 14%. The O concentration, a measure of the completeness of hydrotreating, was consistent at 1.0–1.4 wt%. This is slightly higher than the levels seen in Howe et al. [19], where the O concentration was less than 1.1 wt% for all feedstocks, and in many cases less than 1%. The slightly lower deoxygenation efficiency may have been due to the hydrotreater being operated at slightly lower pressure (1500 psi vs. 1550 psi previously). Deoxygenation is a function of process severity, with higher temperatures and pressures and lower space velocities resulting in a more deoxygenated fuel [25]. Almost no inorganic compounds were detected in the fuel oil, with S and Si being the only two species detectable by ICP-OES (see Table S-4). These compounds were most likely carried over from the sulfided catalyst and the silicon glass wool supporting the catalyst beds. The

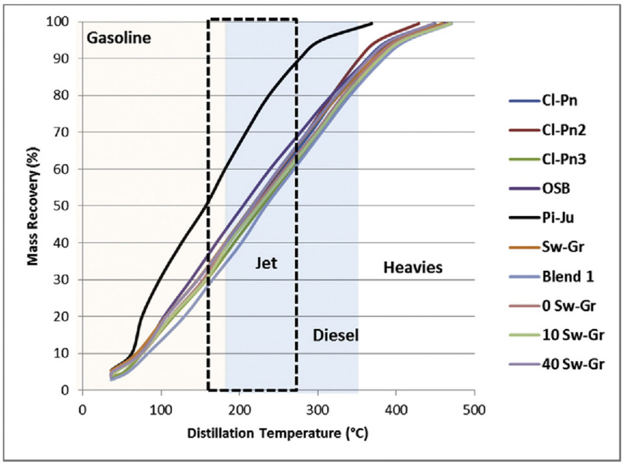

Fig. 2. Simulated distillation results of the upgraded oils. Dashed box represents the jet fuel fraction, which overlaps the gasoline and diesel fractions.

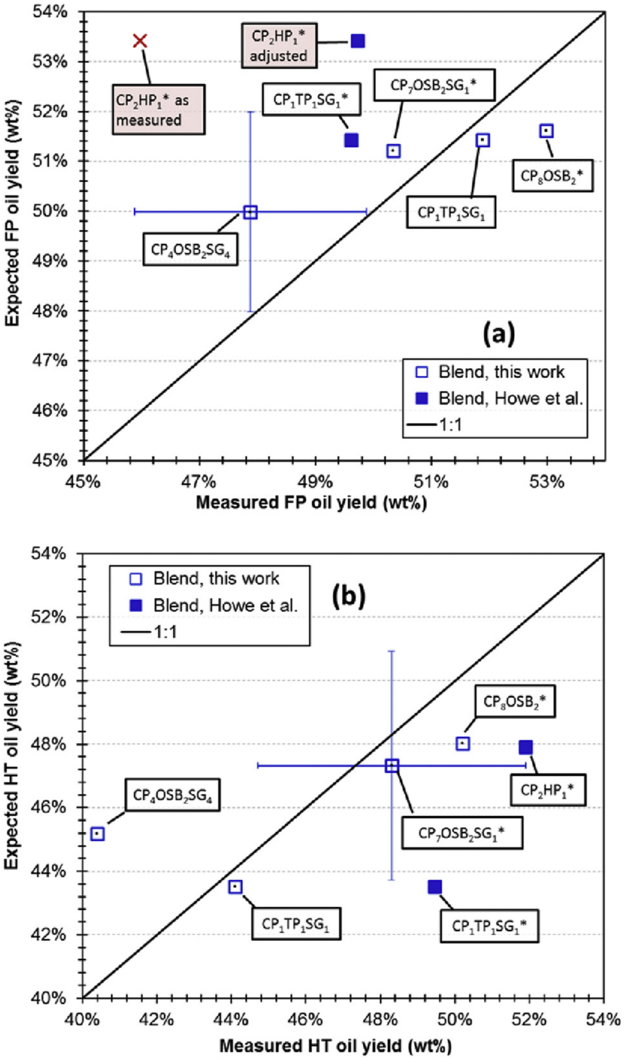

Fig. 3. Comparison of the measured fast pyrolysis (a) and hydrotreating (b) yields of the feedstock blends with yields that would be expected based on the individual blend components. Uncertainty is similar for all measurements and shown for one sample as an example.

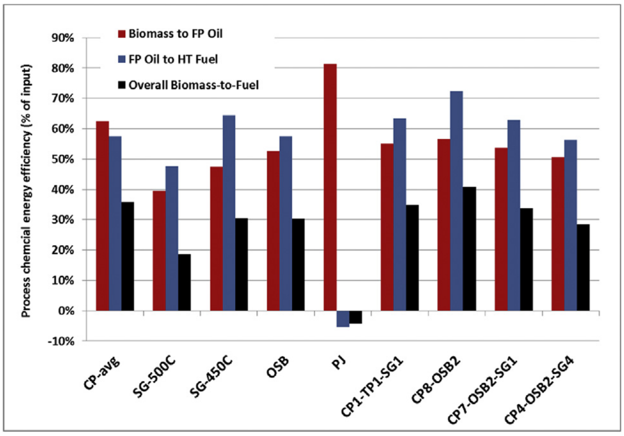

Fig. 4. Energy efficiencies (LHV basis) for converting biomass to FP oil, FP oil to HT fuel, and the overall FP + HT process.

energy content of all fuel oils, measured as the higher heating value (HHV), was nearly constant, ranging from 43.7 to 44.8 MJ/kg. Water content in the fuel, as measured by Karl Fischer titration, was below the detectable limit of 0.1 wt%, indicating an almost completely non-polar product. Total acid numbers (TAN) and carbonyl titrations were both below detectable limits for all feedstocks, indicating that C═O groups were completely removed as expected. The viscosities of the upgraded oils, measured at 40 °C, ranged from 0.495 (PJ) to 1.18 cP (CP). As a reference, the viscosity of water at 40 °C is 0.653 cP. The low viscosity of the piñon-juniper blendstock further supports the hypothesis that only the light fraction was being hydrotreated, as does the density, which, at 0.77 g/cm^3, was lower than the other feedstocks (0.81–0.84 g/cm^3).

The aqueous phase collected from the hydrotreater was very clean, with less than 1 wt% C or N (see Table S-4 for analyses). Inorganic content was also very low, with S and Si comprising the majority of the minerals observed. The very low levels (<12 ppm) of water-soluble K and Na were probably due to both the use of the hot filter in the pyrolysis stage, resulting in a very low inorganic content of the bio-oil feed, and the tendency of the catalyst bed in the hydrotreater to serve as a filter for inorganics. This is consistent with previous results indicating that the water generated during the hydrotreatment process is very clean, and will not require substantial wastewater treatment [26].

In addition to yields, the final fuel quality is an important consideration for biorefineries. Simulated distillation of the upgraded products, shown numerically in Table 3 and graphically in Fig. 2, show that the fractions of compounds boiling in the gasoline, diesel, and jet ranges were influenced by feedstock (note that the fuel fractions sum to greater than 100% since the definitions of the ranges overlap). The gasoline fraction, representing compounds boiling from 0 to 187 °C, ranged from 40 to 47% except for PJ, which was 61%. Because the gasoline fraction consists of the lightest, most volatile compounds, the suspicion that phase separation was occurring in the hydrotreater is further reinforced. The other fractions showed less variability if the piñon-juniper outlier is removed. For all other feedstocks, the diesel cut (187 °C–345 °C) ranged from 41% (OSB) to 47% (CP). The kerosene (jet fuel) fraction overlaps the gasoline and diesel temperatures from 160 to 266 °C. Piñon-juniper showed a large fraction in this range at 37%, with all other feedstocks ranging from 28 to 31%. All mass volatilized at >345 °C was classified as a "heavies". Piñon-juniper had only 2% in this range due to the aforementioned phase separation, while the remaining feedstocks ranged from 11% (CP) to 17% ($CP_7OSB_2SG_1$).

Although catalyst development is not the focus of this paper, the effects of feedstocks on catalyst lifetime are important for techno-economic analysis and modeling. Agglomerations of coke and char can result in reactor plugging, requiring a system shutdown to remove. When the clean pine bio-oil was hydrotreated, a plug approximately 1 cm in length was formed at the top of the first bed. This plug was minor and easy to remove, with little effect on the catalyst beneath. When pure switchgrass was tested, the plug was

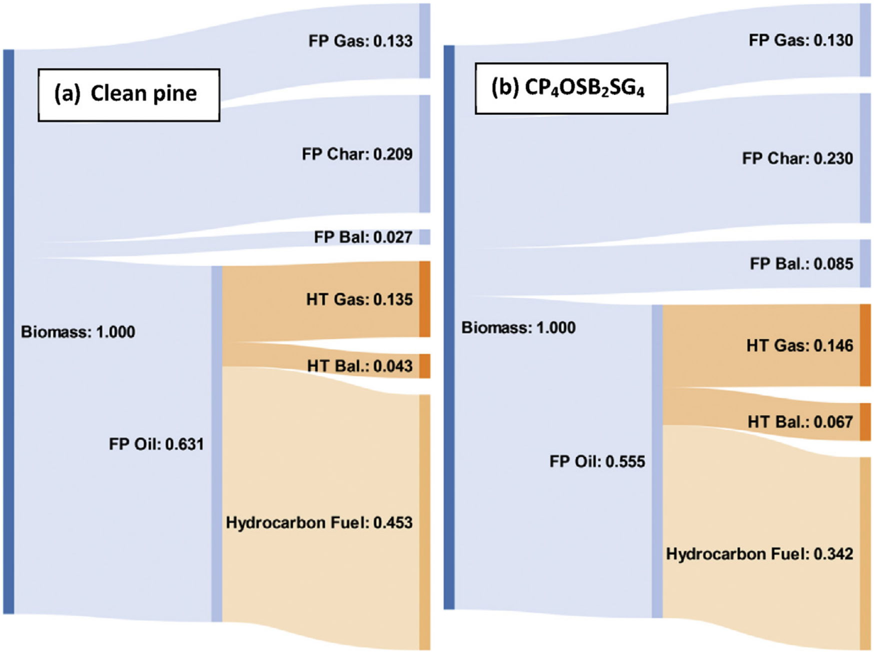

Fig. 5. Distribution of carbon observed from bench-scale fast pyrolysis (blue) and hydrotreating (orange) experiments for (a) pine and (b) the $CP_4OSB_2SG_4$ blend. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approximately 7 cm in length, and the first bed was essentially "glued" together. The switchgrass blends exhibited a plug of approximately 3 cm, with large portions of the catalyst agglomerated together. While qualitative, these results indicate that including large amounts of switchgrass in blends could potentially result in lower catalyst lifetimes.

3.2.3. Impact of blending feedstocks

An important question is whether there are unexpected effects in fast pyrolysis or hydrotreating due to combining feedstocks in blends. To answer this question, various blends of the feedstocks were also tested. The fast pyrolysis and hydrotreating results from the blended materials are shown in Fig. 3 as functions of the yields that would be expected based on the individual blend components. The agreement between measured and expected fast pyrolysis oil yields of the blended materials in Fig. 3a is well within experimental uncertainty, which is estimated to be approximately 2 wt% as explained above. Example uncertainty bars are only shown for one sample to avoid showing multiple overlapping lines. Note that the difference between the replicate $CP_1TP_1SG_1$ samples (Howe et al. and this work) is 2.3 wt%, which is similar to the difference observed between the replicate clean pine (CP) measurements. Another item to note is that adjusting the measured water content of the CP_2HP_1* oil to bring it into agreement with the measured values of the oils from CP replicates and HP also increases the agreement between the expected and measured fast pyrolysis oil contents.

Likewise, Fig. 3b compares the measured hydrotreating (HT) yields of the feedstock blends with the yields that would be expected based upon the individual blend components. As explained above, experiment uncertainty is estimated to be 3.6 wt% for all samples but is only shown for one sample for clarity. Fig. 3b indicates that there may be a slight bias in that five of the six tested blends performed slightly better than expected. However, the measured HT oil yields for the blends are all within the 95% confidence interval (two standard deviations multiplied by the appropriate t-statistic) based upon the expected yields of the blend components. Thus, within experimental error, oil yields from hydrotreatment are considered to be linear functions of the blend components, similar to fast pyrolysis.

3.2.4. Carbon and energy efficiency

The overall carbon and energy efficiency to fuels are important considerations, both for sustainability of a process (efficient resource utilization) and for the economics. It is also important during integrated process development to identify areas for potential efficiency gains.

Fig. 4 shows the energy efficiencies for the main process steps, indicating the fraction of chemical energy in the starting biomass that is retained in the oil during pyrolysis, and the fraction of energy in the bio-oil retained in the fuel blendstock during hydrotreating. For this analysis, the energy content of the hydrogen consumed during hydrotreating has been subtracted from the final fuel blendstock. It should be noted that the contribution from hydrogen consumed during hydrotreating accounts for between 34% (tulip poplar as reported by Howe et al.) and 51% (switchgrass) of the total heating value of the final fuel. Similar to the dry mass and carbon yield values, the efficiencies vary significantly between feedstocks. The pyrolysis step retains between 40% (switchgrass) and 81% (piñon-juniper) of the chemical energy in the biomass feedstock, although all the other feedstocks range between 51% and 65%. In the hydrotreatment step, the energy yield from pyrolysis oil to fuel ranges from 55% (clean pine) to 72% ($CP_{80}OSB_{20}$), except for piñon-juniper, which exhibited a negative energy yield during hydrotreating. This further reinforces the hypothesis that phase separation led to only a lighter, energy deficient fraction of the bio-oil being fed to the hydrotreater. Excluding piñon-juniper, the overall field-to-fuel energy yields, calculated as the product of FP and HT yields, range from 19% (SG_{500}) to 41% ($CP_{80}OSB_{20}$). In general, as reported in Howe et al. as well, the herbaceous feedstocks exhibit lower product and energy yields than the woody materials. However, it is notable that the energy efficiency for switchgrass increased more than 60% when processed at a lower temperature, approaching that of the woody OSB material. The hydrotreating step in this case required less hydrogen and the final product had a higher net energy content. Similar results were observed by Elliot et al. who noted lower hydrogen consumption for corn stover light and heavy oil fractions compared with pine and poplar [27].

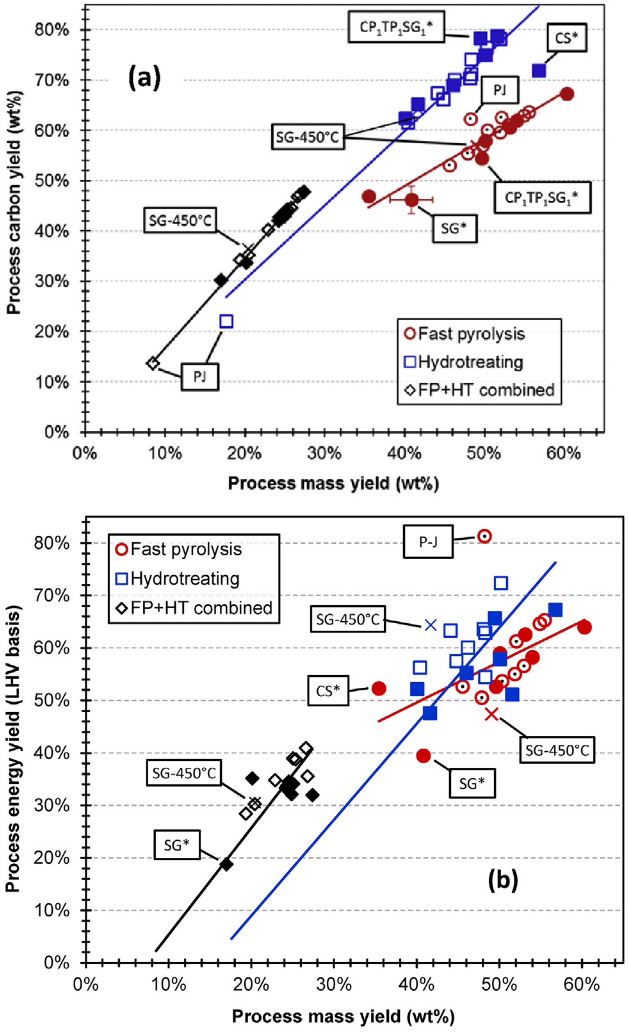

Fig. 6. Process carbon yields (a) and energy yields (b) to liquid products as functions of dry mass yield for fast pyrolysis (FP) and hydrotreating (HT) and combined FP + HT. Results from Howe et al. [19] are shown as solid symbols.

The fate of carbon during thermochemical processing is another important consideration, especially if the byproducts (e.g. char and off-gases) will be combusted for process heat or reformed to generate hydrogen. To visualize this, Fig. 5 compares the partitioning of carbon through the process from biomass to fuel blendstock for the cases of pine and $CP_4OSB_2SG_4$. In this plot, the fast pyrolysis step is shaded blue and the hydrotreating step shaded orange. The amount of carbon unaccounted for in each step is indicated by "FP Bal" and "HT Bal." The solid elemental and gas compositional analyses, shown in Table S-3, were used to calculate

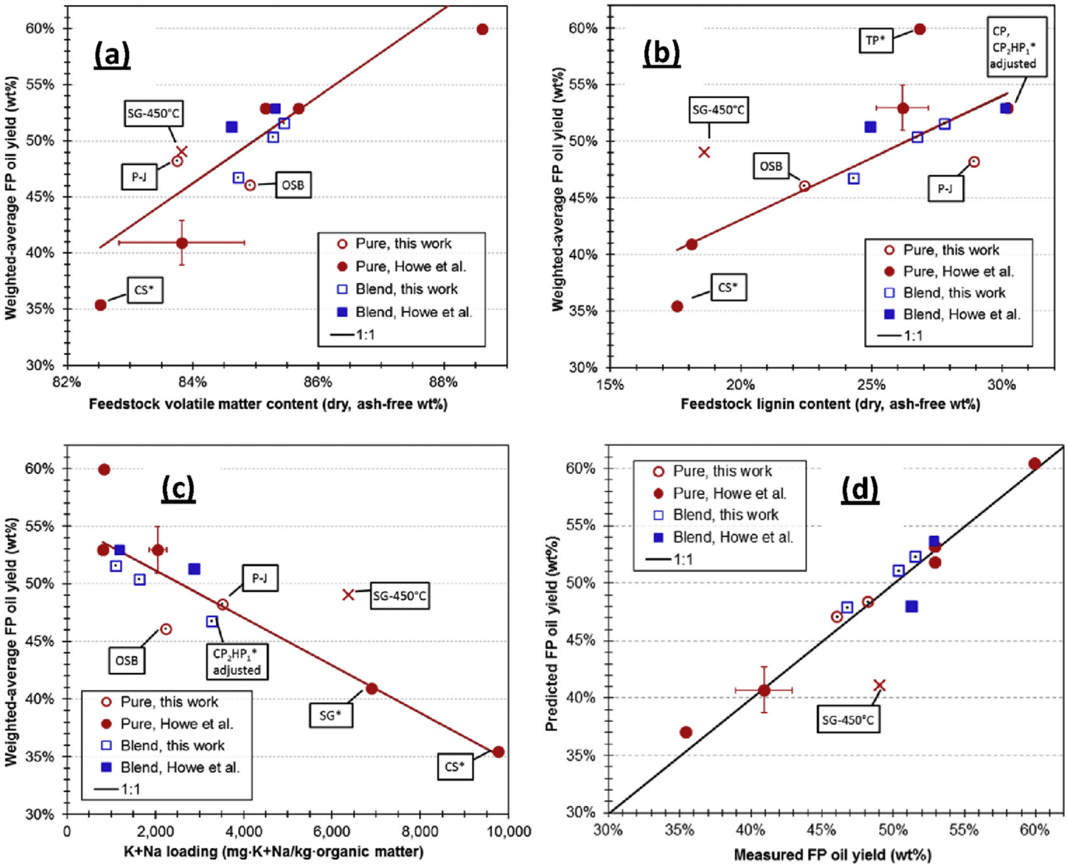

Fig. 7. Example models correlating weighted-average fast pyrolysis oil yields to measured feedstock properties. Figures (a), (b), and (c) exhibit models with volatile matter, lignin, and K + Na contents as single predictor variables, respectively, while (d) shows a multivariate model that uses volatile matter and lignin content.

the partitioning to theses phases. For both the FP and HT process steps, more carbon was partitioned to the liquid phases in the case of pine. More carbon was diverted to char in the blend, and the carbon in the gas was similar for both feedstocks.

Fig. 6a compares the process carbon yield as functions of dry mass yield for each feedstock for fast pyrolysis (FP), hydrotreating (HT), and combined fast pyrolysis and hydrotreating (FP + HT). The graph demonstrates that the relationship between dry mass yield and carbon yield is highly linear for FP and HT for most feedstocks. PJ exhibited a higher carbon yield from fast pyrolysis than expected, while the CS* (corn stover from Howe et al.) demonstrated a lower carbon yield from hydrotreating than expected. Because measuring mass yields of the conversion process has less uncertainty than measuring carbon yields, subsequent results are shown in terms of mass yields. Conversion of mass yields to carbon yields is possible using Fig. 6a and b compares the process energy yield as a functions of dry mass yield for each feedstock for fast pyrolysis (FP), hydrotreating (HT), and combined fast pyrolysis and hydrotreating (FP + HT), reported on an LHV basis. Notably, the relationship between energy and mass yields is not as clear as that of the carbon and mass yields, likely due to the higher uncertainty associated with measuring energy yield, as well as the addition of hydrogen during upgrading.

3.2.5. Preliminary modeling results

Based on the results shown in Fig. 3, it is concluded that, within experimental uncertainty, the fast pyrolysis and hydrotreating oil yields of the blends are weighted linear functions of the blend components. A consequence of this observation is that the yields from blended feedstocks can be treated as replicates of the pure feedstocks to obtain improved yield estimates. In this method, pure feedstocks are treated as blends consisting of 100% of the pure component, and all results are combined in a multivariate model to determine estimates of the oil yields that minimize the sum of the squared errors, assuming the oil yields of the blends are weighted averages of the pure feedstocks. The multivariate calculations are described in Brereton [28], and the results using all of the available data are shown in Table S-5 and Table S-6. The only sample for which the weighted-average fast pyrolysis yield is more than 2% different from the as-determined value is CP_2HP_1*, (−3.2% difference); while the samples for which the weighted-average hydrotreating yields are more than 2% different from the as-determined values are CP_2HP_1* (3.2%), $CP_1TP_1SG_1$* (5.2%), and $CP_4OSB_2SG_4$ (4.9% different).

Relationships between fast pyrolysis yields and feedstock attributes and properties are also of interest; consequently, Fig. 7 a and b plot weighted-average fast pyrolysis oil yields as functions of volatile matter and lignin contents, respectively, on a dry, ash-free basis. The fast pyrolysis oil yield appears to increase with both feedstock properties. The solid lines in Fig. 7a and b are least-square linear fits to the data, and the model parameters are summarized in Table S-6, which shows that the coefficients of determination of the fits (R^2) are 0.73 and 0.65 using volatile matter and lignin contents as the univariate predictor variables, respectively. A similar fit can be obtained between weighted-average pyrolysis oil yields and the sum of potassium and sodium (K + Na), as shown in Fig. 7c. In this model, K + Na is considered to behave primarily as a catalyst, not a reactant, so the quantity of K + Na is considered as a loading and reported in mg of K + Na per kg of dry organic matter. Table S-6 also includes the parameters for fits using total ash, as well as the sum of potassium, sodium, magnesium and calcium. Also shown are example multivariate models using two parameters following the method described by Brereton [28]. The best fit, with an R^2 value of 0.94, was obtained using volatile matter and lignin and is shown in Fig. 7d. Note that the switchgrass test conducted at 450 °C is not included in these regression models but is shown in the plots of Fig. 7 for comparison.

4. Conclusions

Sustainable and cost-competitive biofuel production will likely require a diverse biomass resource base, but performance data at relevant scales for varied feedstocks is lacking. We have reported on an experimental bench-scale study to produce refinery-ready fuel blendstocks via catalytic hydroprocessing (upgrading) of pyrolysis oil using several biomass feedstocks and various blends. Blends were tested along with the pure materials to test the effect of blending on product yields and qualities. Within experimental error, oil yields from fast pyrolysis and upgrading are shown to be linear functions of the blend components. Switchgrass exhibited lower fast pyrolysis and upgrading yields than the tested woody samples, which included clean pine, oriented strand board (OSB), a mix of piñon and juniper (PJ) in the present publication and tulip poplar and hybrid poplar in a previous work. The notable exception was PJ, for which the results from the upgrading process appeared erroneous with a liquid yield of 18%. This was likely associated with the very high viscosity of the PJ fast pyrolysis oil (947 cp), causing a phase separation upon feeding into the hydrotreating reactor. The highest fast pyrolysis yield (54%) was obtained from clean pine (average from three replications), while the highest upgrading yield (50.2%) was obtained from a blend of 80% clean pine and 20% OSB (CP_8OSB_2). The fast pyrolysis and upgrading yields of blends containing switchgrass tended to decrease with increasing switchgrass content. For switchgrass, reducing the fast pyrolysis temperature to 450 °C resulted in a significant increase to the pyrolysis oil yield and reduced hydrogen consumption during hydrotreating, although it did not directly affect the hydrotreating oil yield. The water content of fast pyrolysis oils was observed to increase linearly with the summed content of potassium and sodium, ranging from 21% for clean pine to 37% for switchgrass. Since a major goal of this work is to enable the prediction of conversion performance from properties of the starting feedstock, preliminary multiple linear regression models were developed. These models demonstrate that fast pyrolysis strongly depends ($R^2 \approx 0.94$) on the contents lignin and volatile matter, as well as the sum of potassium and sodium.

Acknowledgements

This work was supported by the U.S. Department of Energy under Contract Nos. DE-AC36-08GO28308 with the National Renewable Energy Laboratory, DE-AC07-05ID14517 with Idaho National Laboratory, and DE-AC05-76RL01830 with Pacific Northwest National Laboratory. Funding was provided by U.S. DOE Office of Energy Efficiency and Renewable Energy's Bioenergy Technologies Office. The U.S Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes. The authors thank Rick French, Kelly Orton, and Scott Palmer for 2FBR operations; Stuart Black and Michele Myers for pyrolysis oil analysis, Kailee Potter for biomass compositional analysis, and David Lee for biomass particle size analysis.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2016.09.012.

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