Fuel xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Characterization of upgraded fast pyrolysis oak oil distillate fractions from sulfided and non-sulfided catalytic hydrotreating

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HIGHLIGHTS

- Comprehensive analysis of catalytically upgraded oak bio-oil.
- Comparison between low oxygen content (LOC) and medium oxygen content (MOC) oils composition.
- Sulfur distribution in the different oil fractions from sulfided and non-sulfided bio-oil derived upgraded oils.

ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form 15 March 2017
Accepted 17 March 2017
Available online xxxx

Keywords:
Fast pyrolysis
Catalytic upgrading
PIONA
Simulated distillation
Oxygen content
Biofuels
Sulfur
Sulfided and non-sulfided catalysts
Distillate fractions
Hydrotreating

ABSTRACT

Catalytic hydroprocessing of pyrolysis oils from biomass produces hydrocarbons that can be considered for liquid fuel production. This process requires removal of oxygen and cracking of the heavier molecular weight bio-oil constituents into smaller fragments at high temperatures and pressures under hydrogen. We present in this paper the characterization of a group of five distillate fractions from each of two types of hydroprocessed oils from oak pyrolysis oil: a low oxygen content (LOC, 1.8% O, wet basis) oil and a medium oxygen content (MOC, 6.4% O, wet basis) oil. The LOC oil was generated using a sulfided hydrotreating system consisting of RuS/C and $xMoS/Al_2O_3$ while the MOC was produced using non-sulfided catalysts, Ru/C and Pd/C. Elemental analysis and ^{13}C NMR (nuclear magnetic resonance) results suggest that the distillate fractions from both oils become more aromatic/unsaturated as they become heavier. Carbonyl and carboxylic groups were found in the MOC light fractions, while phenols were present in the heavier fractions for both MOC and LOC. Paraffin, iso-paraffin, olefin, naphthene, aromatic (PIONA) analysis of the light LOC fraction shows a predominance of paraffins with a minor amount of olefins. Sulfur analysis showed the comparative concentration of sulfur in the different fractions as well as the surprising similarity in content in some sulfided and non-sulfided fractions. These results can be used to direct future research on refinery integration and production of value-added product from specific upgraded oil streams.

1. Introduction

Several routes to produce alternative fuel from biomass have been studied throughout the years [1]. In the thermochemical platform, fast pyrolysis was developed earlier in Europe to produce heat as bio-based boiler fuels [2]. Later, attempts to use raw fast pyrolysis oil, or bio-oil, directly in a refinery showed its incompatibility with most refinery streams due to its high oxygen content [3]. The oxygenates present in the bio-oil cause its acidity, water miscibility, and low heat content as well as thermal and chemical instability—properties that are undesirable for transportation fuel production [4]. More recently, up to 10% bio-oil was reported to have been successfully blended with vacuum gas oil, in a fluid catalytic cracker unit to produce renewable diesel [5]. However, catalytic upgrading through hydroprocessing is still needed to improve bio-oil's processability and production [6] of infrastructure-ready hydrocarbons [3,7].

Bio-oil hydroprocessing uses traditional hydrotreating (HT) catalysts (molybdenum sulfide promoted by nickel or cobalt on

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http://dx.doi.org/10.1016/j.fuel.2017.03.051
0016-2361/

alumina supports) as well as precious metal catalysts [7–10]. Base metals and bimetallic catalysts have also been used [11,12]. Other supports, such as carbon, silica, and zeolites have been tested, using both model compounds [13,14] and actual bio-oil [11,12,15–17]. Unconventional bulk catalysts such as carbides and phosphides have also been explored [18]. Hydroprocessing removes oxygen through a combination of hydrogenation, dehydration, hydrodeoxygenation, decarboxylation, hydrocracking, and other reactions to produce a blend of hydrocarbons that can be fractionated into gasoline, diesel, jet fuel, and heavy fuel fractions. High temperatures and high hydrogen pressures are needed for oxygen removal. However, because of bio-oil's thermal instability, multiple-stage processing is required [7,8,13]. Researchers are seeking a process that optimizes production cost but avoids plug formation, which leads to excessive pressure buildup in the reactor and unplanned process shutdown [19].

Aside from processing considerations, an understanding of the upgraded bio-oil characteristics is necessary to produce an infrastructure-ready liquid product. Characterization of the product will provide a basis on which to select refinery insertion points and subsequent processing and will also generate information that can feed into models that optimize the whole process. The presence of oxygenates in the upgraded oil will depend on the degree of deoxygenation achieved by the hydroprocessing. In turn, the overall cost of the process will be affected by the target deoxygenation level [20]. Other factors, such as catalyst deactivation after longer times on stream, will also result in the presence of oxygenates in the liquid product blend. The presence of oxygenates does not necessarily translate to low refinery fuel blend properties. Indeed, oxygenates (e.g., ethanol) are added to gasoline to improve its auto-ignition/combustion properties [21,22]. However, specific compounds such as dimethylfuran, phenol, and cresol are reported to negatively impact gasoline and diesel quality [23]. Carboxylic acids are unwanted because they can corrode the materials in the current refinery infrastructure. The extent of deoxygenation needs to be optimized and how any incomplete deoxygenation affects the quality/properties of the upgraded biomass-derived oil product should be addressed, because they impact both process and economic considerations in a biorefinery.

In 2011, a seminal publication by Christensen et al. [24] analyzed the distillate fractions of hydrotreated fast pyrolysis oils. This study was important because availability of this information in the literature was limited. In accord with the existing technology at the time of that study, the upgraded oils used were pooled products of several bio-oil hydroprocessing campaigns with various operating conditions. Samples with three different oxygen contents were obtained from composites and then distilled. As expected, the degree of oxygen removal affected the resulting characteristics of each fraction, including heteroatom distribution.

In light of current advances in catalytic upgrading allowing for longer continuous operation [8], analysis of the different distillate fractions was revisited. The previous study [24] reported sulfur concentrations that were much higher than what was expected for woody biomass-derived oils. However, woody biomass has much lower sulfur content than crude oil. Additionally, more recent elemental analysis of hydroprocessed oils using sulfided catalysts typically indicated negligible sulfur concentration. Thus, this study aimed to address this seeming contradiction by using a single batch of pyrolysis oil to eliminate uncertainty due to the starting feed. The effect of sulfur in the catalysts on the final product composition was also tested by using two types of catalysts: (1) ruthenium sulfide supported on carbon extrudate (RuS/C) followed by a commercial sulfided Mo-based catalyst supported on alumina (xMoS/Al_2O_3); and, (2) ruthenium catalyst supported on carbon extrudate (Ru/C) followed by palladium supported on carbon (Pd/C). The hydroprocessing operations produced two oxygen levels. The RuS/C-xMoS/Al_2O_3 catalyst system produced low oxygen content composite oil (LOC) that had about 1.8 wt% O, while the non-sulfided Ru/C-Pd/C catalyst system produced a medium oxygen content composite oil (MOC) with 6.4 wt% O (5.9 wt% O, dry basis). Oxygen-containing functional groups, such as phenols, acids, and aldehydes, were found to be present, along with some moisture. This study also tracked heteroatoms, such as sulfur and nitrogen, in each distillate fraction. Sulfur was found to be in much smaller concentrations than what was previously reported [24].

2. Materials and methods

2.1. Production of pyrolysis oil

The oak-derived pyrolysis oil used in this study was produced using an entrained flow reactor at the National Renewable Energy Laboratory (NREL) at 500 °C. The oil was generated between 10/19/2010 and 11/15/2010, produced at the same time as the oils described in another reference [25]. However, the oil used in this study bypassed the hot vapor filter. Pyrolysis yields were 64% liquid, 24% gas, and 12% char [25].

2.2. Catalysts

Ruthenium and palladium on carbon extrudates were synthesized at Pacific Northwest National Laboratory (PNNL). To remove fines and unwanted water-soluble materials, the carbon extrudates (Norit North America, Norit ROX 0.8 mm) were extensively washed with hot deionized water until the wash water registered neutral pH. The extrudates were then oven dried. Ru/C was prepared using the incipient wetness impregnation method with a commercially available ruthenium nitrosyl nitrate solution (BASF, Ludwigshafen, Germany). The target Ru loading was 7.8 wt%. Pd/C was prepared using palladium acetate (BASF). Synthesis using sodium formate resulted in edge-coated Pd/C catalysts with a target loading of 2.5 wt% Pd. Both catalysts were aged at room temperature after impregnation and finally dried in an oven set at 75 °C under about 1 bar vacuum.

A traditional petroleum HT catalyst (promoted molybdenum oxide on alumina support) was obtained from a commercial vendor and was sulfided for the high-temperature deep deoxygenation.

Activation of catalysts, whether by reduction or sulfidation, was done *in situ*. Reduction of Ru/C and Pd/C was done ultimately at 250 °C under flowing H_2 at operating pressure. Sulfidation was done using a mixture of 35 wt% di-*t*-butyldisulfide (DTBS) in decane at a liquid hourly space velocity (LHSV) of about 0.1 mL sulfiding solution/mL catalyst-h. During the production of LOC oil, about 150 ppm of equivalent sulfur from DTBS was added to the feed bio-oil to ensure that the catalysts remained sulfided during the experiment.

2.3. Reagents

Mixtures and single model compounds were obtained from commercial vendors such as Sigma-Aldrich and Alfa Aesar for identification and calibration purposes. High purity reagent grade chemicals (>99%) were obtained wherever available.

2.4. Production of upgraded oils

Hydroprocessed oils were produced using multi-stage hydroprocessing consisting of (1) pretreatment, (2) low-temperature HT, and (3) high-temperature deep HT and hydrocracking [8]. PNNL conducted all bio-oil hydroprocessing.

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Pretreatment of the pyrolysis oil was done in a continuous, down-flow packed bed reactor loaded with reduced 7.8 wt% ruthenium supported on carbon (PNNL synthesized) under 82 bar of H_2 and at 140 °C. The bio-oil feed LHSV was 0.5 mL bio-oil per mL of catalyst-h. The resulting pretreated bio-oil was the feed to produce the LOC and MOC oils.

For LOC oil production, sulfided Ru/C and commercial HT catalysts were loaded into a two-stage fixed bed (30-mL bed each) reactor system, described in a previous publication [26]. The top sulfided Ru/C bed was maintained at 170 °C–190 °C while the bottom sulfided commercial HT catalyst was maintained at 400 °C. The catalysts were size reduced to −30 + 60 mesh size. The pretreated bio-oil was fed at LHSV = 0.22 mL oil per mL catalyst-h under 123 bar of H_2 flowing at 2000 L H_2/L bio-oil. Average oil yield was 0.50 g oil/g dry feed with average H_2 consumption of 0.060 g H_2/g dry feed.

For MOC oil production, a two-stage non-sulfided Ru/C – Pd/C catalyst system was used. The reactor setup used for this was described in a previous publication [8] and was the same reactor used for the pretreatment. The 440-mL bed reactor contained two precious-metal–based catalysts at 50:50 (vol:vol). The top Ru/C bed was maintained at 170 °C–180 °C while the Pd/C bed was maintained at 395 °C–405 °C. The pretreated bio-oil was fed at LHSV = 0.27 (0.14 total) mL oil per mL catalyst-h under 135 bar of H_2 flowing at 2000 mL H_2/mL bio-oil. Average oil yield was 0.50 g oil/g dry feed with a lower average H_2 consumption of 0.040 g H_2/g dry feed.

2.5. Distillation of upgraded oils

Both LOC and MOC oils were distilled using a bench-scale distillation setup. Cuts were made as follows: (a) fraction 1: 20 °C–150 °C; (b) fraction 2: 150 °C–184 °C; (c) fraction 3: 184 °C–250 °C; (d) fraction 4: 250 °C–338 °C; and (e) fraction 5: >338 °C. Unlike the previous study [24], fractions 4 and 5 were collected under vacuum to prevent oil degradation and coking at higher temperatures. Temperature ranges were 107 °C–198 °C at 6 mmHg and > 198 °C at 6 mmHg for fractions 4 and 5, respectively. Simulated distillation (ASTM D2887) was used to determine the boiling point range for each of the distillate fractions.

2.6. Characterization of distillation fractions

Elemental analysis, water content, and acid number measurements of upgraded oils and fractions were conducted at an outside laboratory (ALS, Tucson, Arizona). Carbon, hydrogen, and nitrogen content were determined following ASTM D5291/ASTM D5373. Sulfur was measured by ASTM D1552/ASTM D4239. Oxygen content was measured by following modified ASTM D5373 for upgraded oils, and by difference for oak pyrolysis and pretreated oils. Moisture content by Karl Fischer analysis was done according to ASTM D6869, and the total acid number (TAN) was measured using ASTM D3339. Other characterizations were done at PNNL. The density and the viscosity of the oil samples were measured using an Anton Paar Stabinger Viscometer SVM 3000. The measurement was done at 40 °C for bio-oils and at 20 °C for upgraded oils. Simulated distillation of the upgraded oils and their fractions was done according to ASTM D2887.

2.7. Modified TAN determination of bio-oils using potentiometric titration

The ASTM standard method D664 for determination of the acid content of petroleum products was modified to measure TAN as a combination of carboxylic acid number (CAN) and phenolic acid number (PhAN). Modifications to the standard method were made to improve the detection of the phenolic content of bio-oils. The method used in this study has been described in the literature [27].

2.8. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis of the samples was performed using an Agilent (formerly Hewlett-Packard) 7890A GC equipped with an Agilent 5975 mass-selective detector. The developed protocol is described in the literature [27].

2.9. Determination of carbonyls in bio-oils by modified Faix method

Carbonyl groups in the oil fractions were measured using the method developed by Faix [28], which was modified to address the long reaction time needed with the Nicolaides method [29]. The modified Faix method used in this study has been described in the literature [27].

2.10. ^{13}C nuclear magnetic resonance (NMR)

The ^{13}C NMR experiments were conducted using a 500 MHz Agilent DD2 spectrometer with a 5 mm Agilent OneNMR Probe. A single pulse sequence used a 45° pulse on the carbon with ^{1}H decoupling during the acquisition (1 s). A 10-s recycle delay was used between pulses and 4000 scans were collected for each sample. The starting pyrolysis oil and pretreated oil were prepared with deuterated dimethyl sulfoxide (d_6-DMSO) while hydroprocessed oil samples were prepared with deuterated methylene chloride (CD_2Cl_2). A relaxant, 0.05 M $Cr(acac)_3$, was added for T_1 reduction and quenching of any residual nuclear Overhauser effect. Inverse-gated decoupling rf pulse sequence was used. The spectra were referenced to internal d_6-DMSO (39.5 ppm) and CD_2Cl_2 (53.19 ppm), as appropriate. The spectra were integrated to obtain carbon mole fractions of the following functional groups: carbonyl, carboxyl, phenolic, aromatic/olefinic, ether and/or alcohol, and paraffinic carbons. The ranges of chemical shifts integrated were carbonyl, 225–200 ppm; carboxyl, 185–170 ppm; phenolic, 170–142 ppm; aromatic/unsaturated, 142–95 ppm; ether, 85–57 ppm; and aliphatic, 52–0 ppm. Integration ranges were adjusted to avoid including the relevant solvent peak.

2.11. Determination of hydroxyl groups in bio-oils using ^{31}P NMR

Phosphorous (^{31}P) NMR has been used to measure –OH present in coal [30,31] and lignin [32–34]. The protocol used in this study has been described in the literature [27]. The regions of peaks used in the measurement were as follows: TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) peak, 175.5 ppm; aliphatic OH, 145–152.0 ppm; phenolic OH, 138–145.0 ppm; carboxylic acid OH, 134.6–138.0 ppm; di-phosphytilated water adduct, 132.8–133.7 ppm; and TPPO (triphenylphosphine oxide) range, 27–29 ppm.

2.12. Determination of paraffins, isoparaffins, aromatics, naphthenes, and olefins

The first three distillate fractions were characterized for gasoline-range hydrocarbon classes following ASTM D6729 for determining individual compounds in spark-ignition engine fuels. Compound identification and classification were conducted using Separation Systems Hydrocarbon Expert 5.10 detailed hydrocarbon analysis software.

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2.13. Determination of oxygenates present by solid-phase extraction GC–MS

Before qualitative GC–MS analysis, oxygenates present in distillate fractions were isolated by solid-phase extraction. Table S-1 in the Supplementary Information contains detailed information on the analysis parameters used in this study. The mass detector was operated in continuous scan mode in the range of m/z 29–600. Compounds detected were identified based on matching with the NIST 2011 mass spectral library using NIST MS Search 2.0 software as well as a visual comparison of reference spectra. No identification was assigned if match quality was below 80% or if the visual comparison of the spectra showed that the compound identified by the library match was erroneous. Relative abundances of compounds were qualitatively compared based on their percentage of the total chromatographic area.

2.14. Determination of volatile aldehydes, carboxylic acids and phenols by high-performance liquid chromatography (HPLC)

Low molecular weight carboxylic acids and phenols were quantified using HPLC after extraction from the hydrocarbon matrix with acidified water. The extraction and HPLC procedures have been reported previously [24]. A list of compounds included in the calibration mixture with their retention times is provided in Table S-2a.

Volatile carbonyl compounds were quantified using HPLC following derivatization with 2,4-dinitrophenylhydrazine (DNPH), as described previously [24] but with modifications as outlined in S-2b. A list of compounds included in the calibration mixture with their retention times is provided in Table S-2c.

3. Results and discussion

3.1. Characterization of oil streams

Oak-derived pyrolysis oil was pretreated using *in situ* reduced Ru/C catalyst and was subsequently hydroprocessed. Two catalytically upgraded products were made: (a) LOC oil that was produced using sulfided catalysts and (b) MOC oil produced using reduced noble metal catalysts. The upgraded oils were subsequently distilled into different fractions. The process is represented schematically in Fig. 1.

Properties of the different oils, namely, oak pyrolysis oil, pretreated oil, and composites of the hydroprocessed oils (MOC and LOC), are summarized in Table 1. The overall catalytic upgrading of pyrolysis oil resulted in 88% deoxygenation for the MOC oil and 96% for the LOC oil. Overall carbon and hydrogen contents increased with the concomitant oxygen content decrease. The calculated O/C and H/C molar ratios are within typical crude oil limits [7,21]. However, the acid number of the MOC is still high compared to refinery standards [21]. The implication of the high acid number in the MOC oil will be further discussed in the succeeding sections.

The small amounts of sulfur and nitrogen in the oils are typical for oils sourced from clean woody biomass. In contrast, algae and agricultural residues tend to have higher amounts of sulfur and nitrogen [35,36]. The volatility of the hydroprocessed oils prevented their analysis at 40 °C; the fractions were thus analyzed at 20 °C. Comparing the two upgraded oils, the trend in viscosity and density follows the trend in oxygen content; i.e., the lower the oxygen content is, the lower are the density and viscosity of the oil [3]. Interestingly enough, the viscosity of the pretreated oil was higher than that of the starting pyrolysis oil. Polymerization reactions of the oak pyrolysis oil upon exposure to high temperatures in the presence of the deactivated Ru/C catalyst are the likely cause of this trend [8,20,37]. Catalyst deactivation of the pretreatment catalyst bed at longer time on stream had already been reported [8].

3.2. Simulated distillation of composite oils

Simulated distillation (SimDis, ASTM D2887) is a GC method that gives an estimate of the fractions of gasoline, jet, diesel, and fuel oil fractions can be recovered from the feed during actual distillation. It is one of the tests that refiners use to evaluate the quality of their crudes. However, with the thermal instability of pyrolysis oils, polymerization of the reactive species results in solids formation [38]. As such, this test was only applied to the hydroprocessed oils. Fig. 2 shows the SimDis curves of both LOC (square) and MOC (circle) composite oils, with standard kerosene (R1608, broken line) and diesel (QCE833, unbroken line) for comparison. The upgraded oil curves straddle and extend beyond the standards, suggesting a mix of components with boiling points in the gasoline, diesel, jet, and heavy fuel ranges. This is similar to what was reported in the literature [15,17,24]. The LOC curve showed that LOC oil contained lighter components (light boilers) compared to the MOC oil. From SimDis data, LOC T_{10}[(1)] is 53 °C while MOC T_{10} is 87 °C. However, LOC has heavier components than MOC as evidenced by its higher T_{90} of 394 °C, compared to the MOC T_{90} of 372 °C. Investigating the nature of these heavier components is currently underway. Curve-fitting determined the preliminary percentage of the different fractions in the composite oil: LOC has 19.5 wt% of constituents with boiling points > 340 °C while MOC has 16 wt%.

3.3. Fractionation of the upgraded oils

Several insertion points within the refinery are considered as potential introduction points of partially or fully converted pyrolysis oils [7,20]. However, it is important for refiners to understand what the composition of these upgraded oil streams is and how these oils might impact their process requirements. On the other hand, a better understanding of the upgraded oil products will inform bio-oil producers how to tailor the liquid fuels properties. Thus, we aim to elucidate the different functionalities present in the bio-oil fractions generated by distillation.

Both atmospheric and vacuum crude oil distillation are used to separate petroleum into several boiling cuts that are further treated to produce petroleum products for market consumption. Gasoline, jet, diesel, and heavy fuels are derived from blending of several refinery streams as well as some additives to achieve target quality metric requirements. Boiling point ranges for each are typically codified in ASTM standards as follows: (1) gasoline (ASTM D4814): T_{10} = 50 °C–70 °C (max), T_{50} = 77 °C (min), 110 °C–121 °C (max), T_{90} = 185 °C–190 °C (max), endpoint maximum = 225 °C; (2) jet (ASTM D1655): T_{10} = 205 °C (max), endpoint maximum = 300 °C; (3) diesel (ASTM D975): T_{90} = 282 °C (min) and 288 °C–338 °C (max); and (4) gas oil: higher than 338 °C. The ranges of values bracket the different classes of fuel grades specified in these ASTM standards. The LOC and MOC oils were fractionated into five fractions, as follows:

a) fraction 1: 20 °C–150 °C, atmospheric
b) fraction 2: 150 °C–184 °C, atmospheric
c) fraction 3: 184 °C–250 °C, atmospheric
d) fraction 4: 250 °C–338 °C (atm.), vacuum applied (107 °C–198 °C @ 6 mmHg)

[1] Tx is the temperature at which x wt% of the sample was evaporated at 101.3 kPa (760 mmHg).

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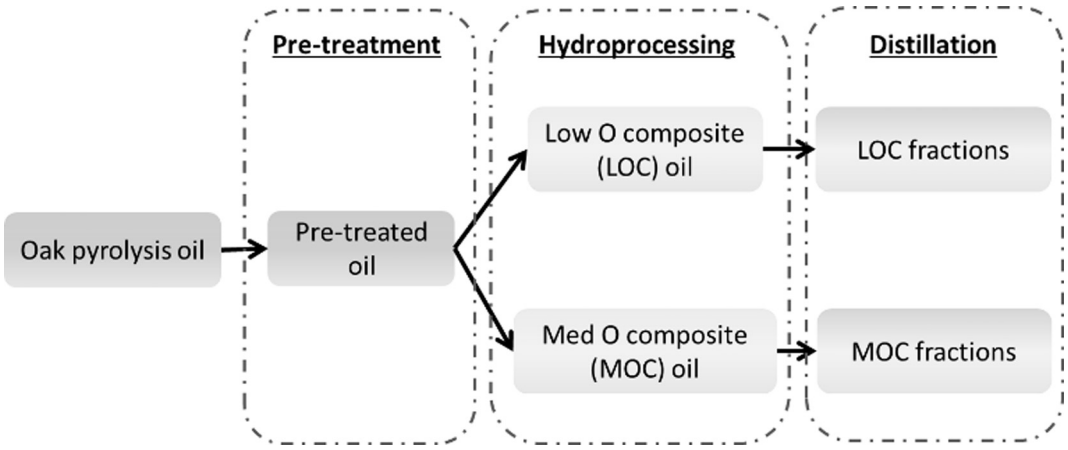

Fig. 1. Production schematic of oils characterized in this study.

Table 1
Characterization of the starting pyrolysis oil, pre-treated oil and composites of the hydrotreated oils.

	Oak pyrolysis oil	Pre-treated oil	MOC composite oil	LOC composite oil
Carbon (D5373/D5291), dry wt%	45.20	56.92	81.88	84.91
Hydrogen (D5373/D5291), dry wt%	7.09	6.72	12.25	13.26
Nitrogen (D5373/D5291), dry wt%	0.07	0.07	<0.05	<0.05
Oxygen (D5373 mod), dry wt%	47.70	36.34	5.87	1.84
Sulfur (D4239/D1552), dry wt%	<0.02	<0.02	<0.03	<0.02
O/C molar ratio	0.79	0.48	0.05	0.02
H/C molar ratio	1.88	1.42	1.80	1.87
Water content (KF, ASTM D6869), %	19.1	20.35	0.6	<0.3
TAN (ASTM D3339), mg KOH/g oil	106.9	109.7	39.3	<0.01
Density, g/cc	1.24 (40 °C)	1.23 (40 °C)	0.87 (20 °C)	0.83 (20 °C)
Viscosity, mm^2/s	113.71 (40 °C)	160.77 (40 °C)	2.67 (20 °C)	1.82 (20 °C)

Note: Average standard deviation for the duplicate elemental analysis results are 0.06, 0.21 and 0.20 wt% for C, H, and O, respectively.

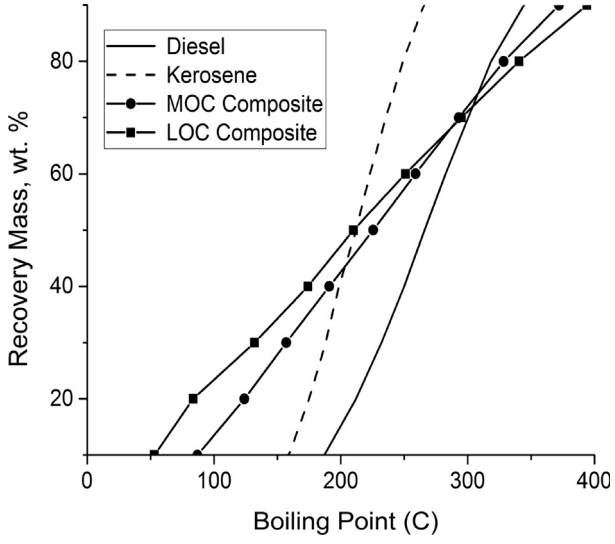

Fig. 2. Simulated distillation of LOC (low oxygen containing) and MOC (medium oxygen containing) composite oils.

e) fraction 5: >338 °C (atm.), vacuum applied (>198 °C @ 6 mmHg).

Vacuum was applied for distillation at temperatures higher than 250 °C to prevent solids formation due to cracking reactions at very high distillation temperatures [21]. Fractionating the composite oils into these groups allows for analysis of the various boiling ranges that may ultimately comprise the gasoline (fractions 1 and 2), jet (fractions 2 and 3) and diesel (fractions 3 and 4) fuel ranges. The difference in the boiling point ranges between fractions of reference [24] and the current data set, as well as differences in pyrolysis oil upgrading precludes direct comparison. For both LOC and MOC distillations, total liquid recovery of the different fractions was 99% from the starting feed. The amount of each fraction based on SimDis data is given in Table S-3.

3.4. Elemental analysis of upgraded oil fractions

Fig. 3 depicts the elemental analyses for each of the LOC and MOC fractions. Table S-4 presents the same information in tabular form. As can be seen from (a), the carbon content of LOC oil fractions increased as the fraction became heavier with higher boiling range. Concomitantly, the hydrogen content decreased (15.5 wt% to 11.4 wt%) while the oxygen content (1.1 wt% to 1.2 wt%) remained almost the same. The Karl Fischer method (ASTM D6869) did not detect water. The molar H/C ratio decreased from 2.2 to 1.6 from LOC fraction 1 to LOC fraction 5, suggesting that the heavier fractions are more unsaturated than the lighter fractions. Oxygen was present in almost equal amounts in the LOC fractions. In comparison, the MOC oil fractions exhibited the same trend as the LOC ones of increasing carbon content and decreasing hydrogen content as the fractions become heavier. However, with the higher oxygen content in the starting composite, the oxygen content of each fraction varied. The MOC fraction 2 contained the highest amount of oxygen, followed by MOC fraction 1, 11.0 wt% and 10.2 wt%, respectively. Oxygen content decreased from MOC fraction 3 to MOC fraction 5 (7.1 wt% to 2.3 wt%). Water was only detected in MOC fraction 1. The trend in the molar H/C ratio in the

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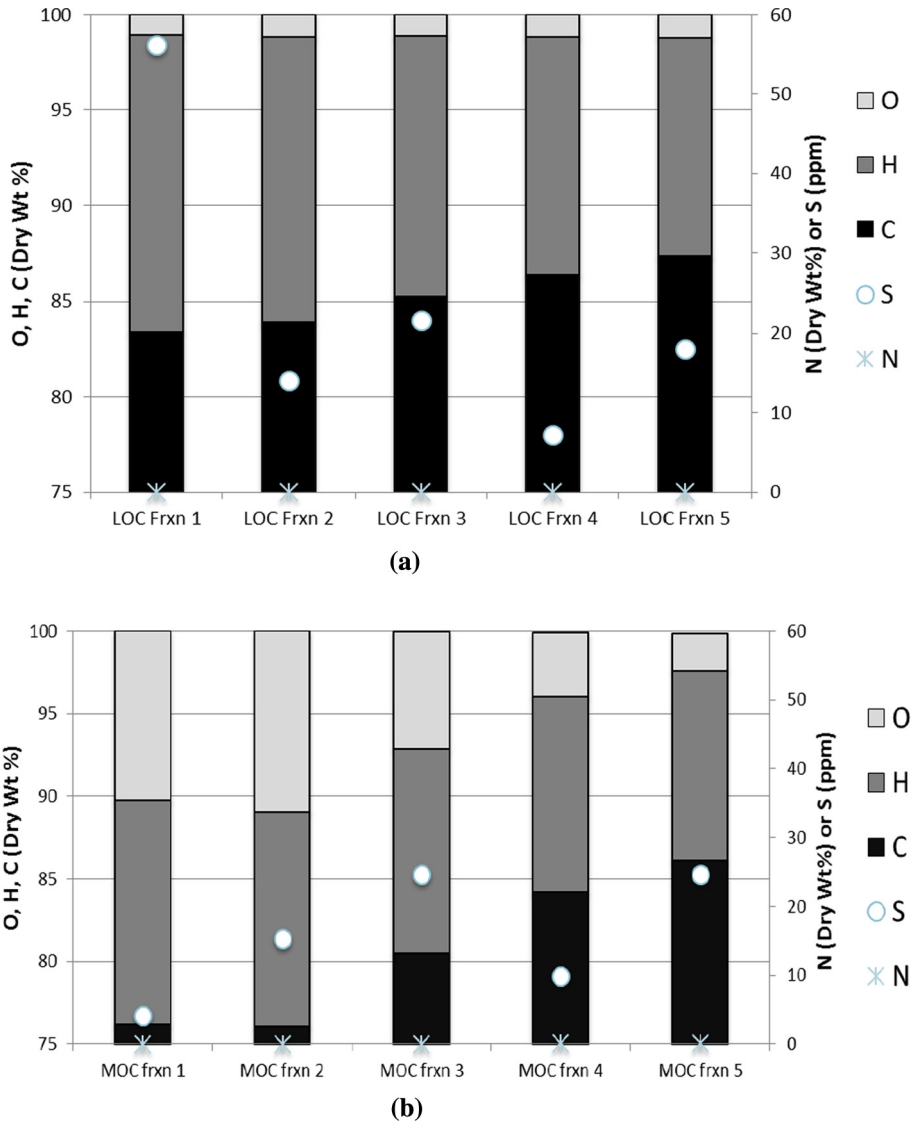

Fig. 3. Elemental composition of the different fractions: (a) LOC (low oxygen containing) oils, (b) MOC (medium oxygen containing) oils.

MOC oil fraction was similar to that of the LOC oil fractions, decreasing from 2.14 to 1.60 from fraction 1 to fraction 5.

Fig. 4 shows the van Krevelen plot of the various fractions. With unchanging oxygen content, the molar H/C ratio of the different fractions was independent of the molar O/C ratio for the LOC oils. For the MOC oil fractions, a linear trend between H/C and O/C was observed. Though it may be considered intuitive, as of press time, this is the first time that such a trend has been reported for hydroprocessed fast pyrolysis bio-oil fractionated cuts. If a correlation between H/C and O/C of different oil cuts can be established based on processing conditions, a single CHN analysis may be sufficient to give a snapshot of the product quality during operation.

The content of other heteroatoms (i.e., nitrogen and sulfur) is also shown in Fig. 3. These are minor constituents. Because these compounds can affect both further processing and meeting fuel specifications, tracking their presence in the fractions is important. For the most part, nitrogen content was below detection level except for MOC fraction 4 and MOC fraction 5 (see Table S-4). The heavier fraction contained twice as much as the less heavy fraction (0.08 wt% vs. 0.18 wt%). These nitrogen content levels are comparable to that reported for West Texas Intermediate, Arabian Light, and Arabian Medium crudes at the low end and Arabian Heavy and Kuwait Export at the high end [22]. For ppm-level sulfur analysis, ASTM D5453 was used. The presence of sulfur in different boiling ranges suggests that various types of sulfur are present in the upgraded oil. The same conclusion was found in the paper by Christensen et al. [24], although our reported values are much lower. There is an ongoing effort to identify these sulfur species, although the very small amount presents a challenge in categorizing the functionality of the sulfur present. We hypothesize that the sulfur functionalities might range from light mercaptans to the more recalcitrant substituted benzothiophenes, similar to what has been reported for petroleum-based fuel, based on their presence in the heavier boiling fraction [39]. It will be of interest to trace whether the heavier components were originally from the biomass source or whether these were formed under these processing conditions.

Discounting the fraction 1 of both LOC and MOC oils, the amount of sulfur per fraction was almost the same for both upgraded oils. Fraction 3 (184 °C–250 °C) and fraction 5 (>338 °C) had the largest amounts at 21.7 (LOC) and 24.6 (MOC) ppm and 18 (LOC) and 24.6 (MOC) ppm, respectively. The fraction recovered at the diesel boiling point range, fraction 4 (250 °C–338 °C), showed 7.2 and 9.8 ppm for LOC and MOC oils, respectively. These

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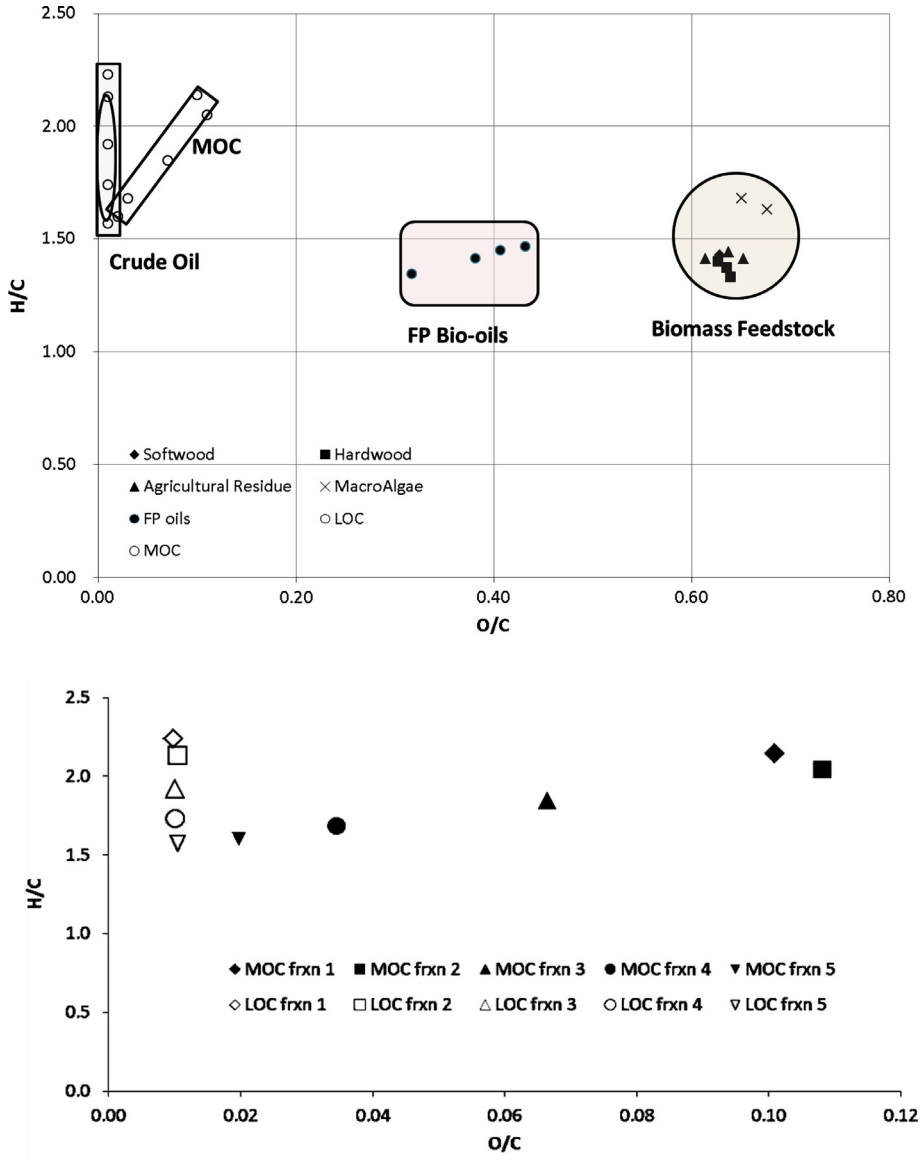

Fig. 4. van Krevelen plot of the resulting oil fractions.

values are below the ultra-low-sulfur diesel threshold of 15 ppm. The effect of sulfided and non-sulfided catalysts was observed in comparing fraction 1 of both oils. For LOC oils, the lightest fraction contained the highest reported sulfur concentration (56.2 ppm). The high content may be due to dissolved H_2S and light mercaptans that were by-products of the catalyst sulfidation as well as sulfur incorporation into the lighter bio-oil product. In the refinery, the entrained H_2S and light mercaptans are typically removed by alkali wash after the gasoline hydrotreater. On the other hand, the MOC fraction 1 contained the lowest sulfur concentration at 4.1 ppm. Considering that the MOC oil was produced with the use of non-sulfided catalysts, it is likely that the sulfur in the final product is due to sulfur that was initially present in the bio-oil feed.

3.5. Simulated distillation of the upgraded oil fractions

Each of the LOC and MOC oil fractions was subjected to ASTM D2887. Fig. 5 shows the SimDis results for both the LOC and MOC fractions based on the measured initial boiling point (IBP, considered to be at 0.5% mass recovered), T_{10}, T_{50}, T_{90}, and endpoint. Fraction 1 of both oils shows that the upgraded oils contain light compounds, with LOC having IBP and T_{10} less than the lowest measurable temperature of the method used. In comparison, only the IBP for MOC was not measurable, corroborating the observation in the previous section that LOC oil has lighter (lower boiling) components than MOC oil. Fraction 2, with a target distillation range of 150 °C–184 °C, did not satisfy gasoline T_{10} specifications, mainly because fraction 1 was already removed. However, with an endpoint temperature of 220 °C, LOC fraction 2 can conceivably be blended with LOC fraction 1, potentially resulting in a fraction that can satisfy gasoline specifications. Both LOC and MOC fraction 3 are within the boiling point requirements for jet A. For the diesel specification, LOC fraction 4 fulfilled the boiling point requirements, but MOC fraction 4, with T_{90} = 339.5 °C, has a slightly higher value than the 338 °C maximum. As with LOC fraction 2, blending with other streams can further minimize the slightly higher T_{90} value of MOC fraction 4. It must be noted that other characteristics, such as elemental (discussed in the previous section) and functional group (discussed next) composition, also determine whether a fraction can be considered as an attractive fuel blend. For example, although oxygen is not specified in ASTM

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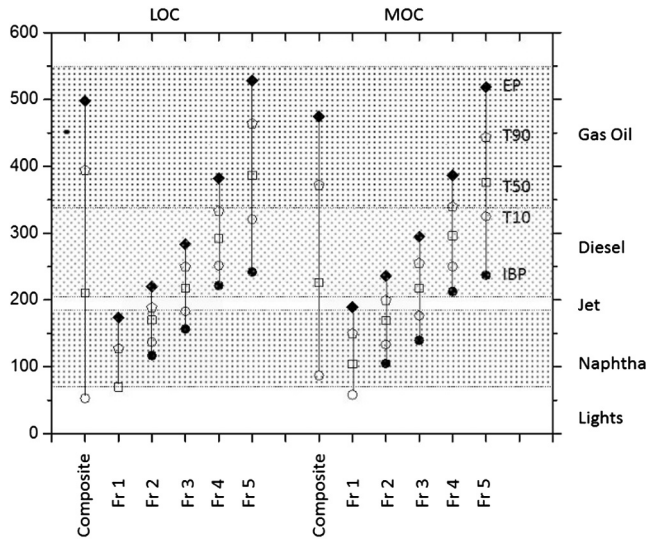

Fig. 5. Upgraded oil fractions distillation ranges in comparison to target fuel ranges.

fuel specifications, the oxygen content is limited by the Environmental Protection Agency (EPA) in the United States. Under the Clean Air Act, gasoline used in the United States must be "substantially similar" to fuel used to certify vehicles for emissions requirements [40,41]. The EPA has determined that gasolines containing aliphatic ethers and alcohols and their mixtures are substantially similar when blended to a concentration equivalent to 3.7 wt% oxygen (10 vol% ethanol). Based on these limitations, the MOC fractions would not meet the "substantially similar" definition without further HT or other treatment to remove oxygenates.

Drivability index is an indication of a fuel's cold-start and warm-up drivability. Lower values predict better performance [42]. According to a 2009 Chevron Corporation technical review, the typical U.S. range is between 375 and 610 while the Asia-Pacific region range is between 460 and 580 [42]. ASTM D4814 limits this value to a maximum of 597. ASTM D86 was performed to calculate the drivability index of fraction 1 for both LOC and MOC. LOC fraction 1 has 463 while MOC fraction 1 has 542. Both fractions pass the drivability index requirement.

3.6. ^{13}C NMR

The summary of the carbon functional groups present in the various fractions as determined by ^{13}C NMR is illustrated in Fig. 6 and summarized in Table S-5. For LOC fractions, only aliphatic, phenolic, and aromatic/unsaturated double bond groups were detected by ^{13}C NMR. The amount of aliphatics decreased as the aromatic content increased. This trend is in agreement with the earlier observation of decreasing molar H/C ratio as the fractions became heavier. ^{13}C NMR data suggests that about 18.2% of the carbon in the jet fuel fraction (LOC fraction 3) comes from aromatic compounds while about 23.4% of the carbons in the diesel fraction (LOC fraction 4) are considered aromatic carbons. Phenolic groups were also found to increase from 0.2% to 5.6% of the carbons from LOC fraction 1 to LOC fraction 5.

Similar trends in the aliphatic, aromatic, and phenolic groups in the MOC fractions were also observed. Additionally, carbonyl, carboxyl, and ether/alcohol groups were also detected in these fractions. These functional groups were only found in the lighter fractions (i.e., MOC fraction 1 to MOC fraction 3). MOC fraction 1 contained the largest amounts of carbonyl and ethers, while MOC fraction 2 contained the highest quantity of carboxylic groups. This trend was corroborated by the results of the HPLC method below.

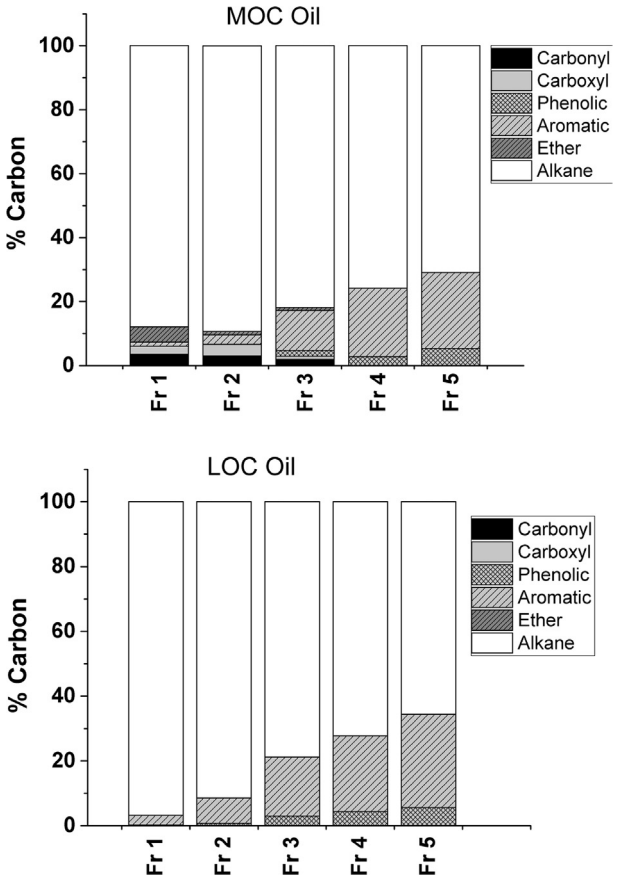

Fig. 6. Carbon functional group distribution in the hydroprocessed fractions by ^{13}C NMR.

The presence of these oxygenated compounds, especially the acids, will preclude direct introduction of the unmodified fractions into a gasoline engine due to possible corrosion issues [43].

3.7. Acid content

The various TAN values of the fractions are reported in Table S-6. Only the MOC fractions contained reportable acid content; values in decreasing order were 116.6 mg KOH/g oil in MOC fraction 2, followed by MOC fractions 1, 3, 4, and lastly, fraction 5 with 0.3 mg KOH/g oil. There was a good agreement between the TAN values generated by the external laboratory and the TAN values generated using the modified protocol at PNNL, suggesting that these fractions contain mostly carboxylic acids [44]. Recovery values (defined as ratios of the results of the PNNL-modified TAN protocol and ASTM D3339 test) were between 93% and 107%.

The fractions were analyzed by HPLC to quantify the acids and phenols present in the fractions. However, meaningful results were only determined in fractions 1 to 3 for both LOC and MOC oils. The specific acid and phenol compounds used as standards in the method were not identified in fractions 4 and 5 in meaningful quantities. Acids that were accounted for include C_1 to C_6 carboxylic acids while phenolic compounds accounted for include phenol, o-cresol, m-cresol, p-cresol, and 2-ethylphenol. Results are summarized in Table S-7. As shown, the most abundant acids, in decreasing order, were iso- and valeric acids > iso- and butyric acids > acetic acid. MOC fraction 2 contained the largest amount of quantified acids among the analyzed samples while LOC fraction 2 contained the highest amount of quantified phenol (i.e., o-cresol).

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This will impact the utility of unrefined LOC fraction 2 as a direct blend for gasoline.

3.8. Carbonyl content

The modified Faix method [27,45] was used to quantify the carbonyl content in the oil fractions. From ^{13}C NMR, we know that MOC oils have peaks in the carbonyl region. Carbonyl titration results, shown in Table 2, corroborate this observation. Carbonyl content was found to decrease as the MOC fraction becomes heavier.

Table S-8 lists the various aldehydes that were identified and quantified using HPLC in the LOC and MOC fractions. In comparison with acids and phenols, aldehydes were present in much smaller amounts. MOC fractions tended to contain more aldehydes than their corresponding LOC fractions. The most abundant aldehyde in all fractions was benzaldehyde in MOC fraction 1, followed by 2,5-dimethylbenzaldehyde in MOC fraction 2.

3.9. Gas chromatography/mass spectrometry

All fractions were analyzed by GC–MS. Note that reported values from GC–MS analysis in this paper are only semi-quantitative at best, based on area count. Only compounds with higher than 80% match with the GC–MS database were reported. As the fraction became heavier for both LOC and MOC oils (i.e., fraction 4 and fraction 5), the GC–MS database included in the analytical software package became mostly inadequate for identifying the compounds. As such, only fractions 1–3 results are reported here.

The GC–MS analysis categorized the compounds into several nonpolar and polar classes: n-paraffin, isoparaffins, aromatic, naphthenes, olefins, phenol, alcohol, ester, acid, furan and pyran (data not shown). Naphthenes and aromatics are the most abundant classes of compounds in LOC and MOC fractions 1–3. Aromatics tend to increase as the fraction becomes heavier—also corroborated by ^{13}C NMR data. On the other hand, naphthenes decrease with increasing boiling point range. LOC fractions contain much higher amounts of paraffins than the MOC fractions. Similar to naphthenes, the paraffins (n- and iso-) tend to decrease with increasing boiling point range. As high as 40 area% of the samples, found in MOC-3, was unidentifiable based on the available database.

Polar compounds were mostly found in the MOC fractions. A composite of 1-butanol, 1-pentanol, and 1-hexanol comprised about 63 and 21 area% of the oxygenates in MOC fraction 1 and MOC fraction 2, respectively. Unsubstituted organic acids (acetic, propanoic, and butanoic acids) were only found in MOC fraction 1 at 17 area% by GC–MS. In contrast with the HPLC result, no acetic or propanoic acids were identified in MOC fraction 2. However, GC–MS suggests that it contained unsubstituted and methyl-substituted butanoic and pentanoic acids at 24 area%. For fraction 3, phenols were found to be the dominant oxygenates, at 55 area% for MOC and 87 area% for LOC. Considering that phenols tend to be more recalcitrant than other types of oxygenates during hydroprocessing [3,13], it is not surprising that they are pervasive in the MOC and LOC fractions.

LOC fractions 1 and 2 contained only phenolic compounds, while LOC fraction 3 had minimal amounts of ethers and esters as well as some unidentified polar compounds. Methyl-substituted phenols were the most abundant phenolic compounds (59 area%) in LOC fraction 1, consisting of three compounds; namely, 2-, 3- and 4-methylphenols (in decreasing relative area% content, data not shown). On the other hand, C_8 (dimethyl- and ethylphenols) are the most abundant oxygenates in LOC fraction 2 while C_9 compounds (ethyl-methyl-, methylethyl-, and trimethylphenols) and C_{10} compounds are the most abundant oxygenates in LOC fraction 3.

5.4. ASTM D6729 – PIONA analysis

Functional group analysis of petroleum fractions gives insight into their behavior during processing [46]. ASTM D6729 (PIONA analysis) looks at the paraffins, isoparaffins, olefins, naphthenes, and aromatics present in the lightest LOC and MOC fractions. Table 3 summarizes the results of the light fractions analysis. Based on these values, derived research octane number (RON) and motor octane number (MON) were also estimated using Hydrocarbon Expert v.5. The values reported for LOC and MOC fraction 1 are within the ballpark of reported RON values for unblended naphtha cut coming out of the refinery distillation column. Compared to LOC fraction 1, MOC fraction 1 has more unidentified compounds.

ASTM D6729 has its limitations. The method states that it is "applicable to samples containing less than 25% by mass of olefins." Additionally, co-elution is possible, especially between olefins and C_7 and higher saturated compounds. The method is only applicable to compounds with boiling points below 225 °C

Table 2
Functional group characterization of the various oil fractions.

	Low Oxygen Content					
	Composite	Frac. 1	Frac. 2	Frac. 3	Frac. 4	Frac. 5
Carbonyl concentration (mmol/g)	BDL*	0.14	BDL*	BDL*	0.10	BDL*
TAN (mg-KOH/g)	BDL*	BDL*	BDL*	BDL*	BDL*	BDL*
Hydroxyl determination (mmol/g)						
Aliphatic – OH	BDL*	BDL*	BDL*	0.43	BDL*	0.02
Aromatic – OH	0.10	0.10	BDL*	0.1	0.95	0.05
Carboxylic – OH	BDL*	BDL*	BDL*	0.1	BDL*	BDL*
	Medium Oxygen Content					
	Composite	Frac. 1	Frac. 2	Frac. 3	Frac. 4	Frac. 5
Carbonyl concentration (mmol/g)	1.1	1.67	1.53	1.03	0.63	0.34
TAN (mg-KOH/g)	39.1	51.2	122.6	41.9	5.1	BDL*
Hydroxyl determination (mmol/g)						
Aliphatic – OH	0.33	0.68	0.24	0.14	BDL*	BDL*
Aromatic – OH	0.44	0.01	0.08	0.96	0.94	0.43
Carboxylic – OH	0.31	0.74	1.38	0.73	0.08	0.01

* BDL – Below detection limit.

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Table 3
PIONA (paraffin, iso-paraffin, olefin, naphtha, aromatic) characterization of light fractions.

Group	LOC fraction 1 (% vol)	LOC fraction 2 (% vol)	MOC fraction 1 (% vol)
Paraffin	44.4	21.0	12.9
iso-paraffins	14.0	14.8	12.7
Aromatics	2.8	19.6	2.1
Naphthenes	36.7	30.6	43.9
Olefins	1.6	4.8	1.9
Unidentified	0.5	9.2	14.6
Benzene	0.5	0.0	0.1
RON	65	38	78
MON	60	41	59

and is not robust in handling heteroatoms aside from methanol, ethanol, t-butanol, methyl t-butyl ether, ethyl t-butyl ether, and t-amyl methyl ether. As such, the analysis reported high amounts of unidentified components in MOC fraction 1 and was not applicable to analyze MOC fraction 2.

Recent work by Huber et al. used nitric oxide ionization spectroscopy evaluation (NOISE) to identify the functional groups present in the whole organic fraction collected after pyrolysis oil hydrotreatment [47]. The authors reported an overwhelming amount of naphthenes—about 90 wt% of their total organic product. Though higher than the amount we reported, the naphthene in the light and naphtha fractions of the low oxygen content oil in [24] was 46–52 vol%. For comparison, samples were also sent to Triton Analytics for analysis. Results using NOISE (data not shown here) revealed a higher amount of naphthene in the samples, e.g., 71 wt% using NOISE vs. 40 wt% (37 vol%, Table 3) using ASTM D6729 for LOC fraction 1. NOISE analysts pointed out the method's limitation with lighter compounds, i.e., it does not report compounds having lower than C_5. Additionally, the database from which the evaluation is determined was developed using petroleum-based compounds. Further inquiry into the method suggested the potential for GC–MS to have a bias towards naphthenes, consistent with the result reported in the previous section. Aside from the method, other possible reasons for the discrepancy between our data, [24], and [47] include inherent differences in the starting pyrolysis oils, HT catalysts, and conditions as well as boiling point ranges of the fractions analyzed.

3.11. Carbonyl titration, CAN/TAN and ^{31}P NMR

The composite oil and the distillate fractions were also analyzed using methods developed in the collaborative project between PNNL and NREL; Table 2 summarizes this data. As expected, the LOC oil had a very small amount of oxygenates present. The carbonyl values reported for fractions 1 and 4 are within the error of the procedure. On the other hand, fractionated MOC oil had high carbonyl contents in fractions 1 and 2, corroborating the HPLC data above. The low acid content of the LOC samples was not amenable to accurately differentiating the end points for carboxylic and phenolic fractions of the oil. Indeed, other analyses done in this study suggest that the TAN of the LOC samples is derived from phenolic rather than carboxylic acids. For MOC, fraction 2 had the highest TAN value while the heaviest oil fraction (fraction 5) has no appreciable amount of acids. Carboxylic data from ^{31}P NMR data corroborates the trend seen in the CAN/TAN analysis.

4. Conclusions

We have conducted a comprehensive characterization of distillate fractions from hydroprocessed bio-oils produced at two different oxygen contents. The approach used in this effort allowed for traceability of the data to the upgrading process used. We reported the presence of recalcitrant sulfur species, independent of the hydroprocessing employed, and showed the effect of using sulfided catalysts on sulfur distribution. The sulfur content was much lower than was previously reported. We also showed the distribution of oxygenates present in the different fractions. LOC fractions 1 and 2 have the potential to satisfy boiling point requirements for gasoline. While this can be true for the same MOC fractions, the presence of acid will likely preclude these from being direct gasoline blendstock. Our results suggest the need to deeply deoxygenate the pyrolysis oils before acids can be removed from the upgraded bio-oil. Additionally, this research contributes to a better understanding of the chemical composition of upgraded oak bio-oil. With input from refiners and chemical manufacturers regarding specific stream requirements, opportunities for valorizing different boiling fractions for use as fuel blendstocks, refinery integration streams, or chemical feedstocks may be more completely identified. Further systematic research on the relationship of various biomass feedstock processing (from a single source, aside from oak, or a combination of other sources) with the composition of the final product will need to be accomplished to complete the picture.

Acknowledgements

The support for this study was provided by the Bioenergy Technologies Office of the U.S. Department of Energy under contract numbers DE-AC36-08-GO28308 and DE-AC06-76RLO-1830. The authors would like to acknowledge the following scientists and engineers for their scientific contributions: Heather Job, Beth Hofstad, Juan Lopez Ruiz, Gary Neuenschwander, Leslie Rotness, Daniel (Miki) Santosa, Craig Lukins, Igor Kutnyakov, and Alan Zacher; Maura Zimmerschied, Deanna Auberry and Kay Hass for technical editing. The authors also wish to thank Dan Villalanti and Joy Cocchiara of Triton Analytics for valuable discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.03.051.

References

[1] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 2006;106:4044–98.
[2] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils: state of the art for the end users. Energy Fuels 1999;13:914–21.
[3] Elliott DC. Historical developments in hydroprocessing bio-oils. Energy Fuels 2007;21:1792–815.
[4] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 2012;38:68–94.
[5] Pinho ADR, de Almeida MBB, Mendes FL, Ximenes VL, Casavechia LC. Co-processing raw bio-oil and gasoil in an FCC Unit. Fuel Process Technol 2015;131:159–66.
[6] Wildschut J, Melián-Cabrera I, Heeres HJ. Catalyst studies on the hydrotreatment of fast pyrolysis oil. Appl Catal B 2010;99:298–306.
[7] Zacher AH, Olarte MV, Santosa DM, Elliott DC, Jones SB. A review and perspective of recent bio-oil hydrotreating research. Green Chem 2014;16:491–515.
[8] Olarte M, Zacher A, Padmaperuma A, Burton S, Job H, Lemmon T, et al. Stabilization of softwood-derived pyrolysis oils for continuous bio-oil hydroprocessing. Top Catal 2016;59:55–64.
[9] Wang H, Male J, Wang Y. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. ACS Catalysis 2013;3:1047–70.
[10] Wildschut J, Iqbal M, Mahfud FH, Cabrera IM, Venderbosch RH, Heeres HJ. Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst. Energy Environ Sci 2010;3:962–70.
[11] Ardiyanti AR, Khromova SA, Venderbosch RH, Yakovlev VA, Heeres HJ. Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a delta-Al_2O_3 support. Appl Catal B-Environ 2012;117:105–17.

[12] Ardiyanti AR, Khromova SA, Venderbosch RH, Yakovlev VA, Melian-Cabrera IV, Heeres HJ. Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. Appl Catal a-Gen 2012;449:121–30.
[13] 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-economical study. Catal Today 1996;29:297–301.
[14] Guvenatam B, Kursun O, Heeres EHJ, Pidko EA, Hensen EJM. Hydrodeoxygenation of mono- and dimeric lignin model compounds on noble metal catalysts. Catal Today 2014;233:83–91.
[15] Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Olarte MV, Zacher AH, et al. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy Fuels 2012;26:3891–6.
[16] Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Zacher AH. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. Environ Prog Sustainable Energy 2009;28:441–9.
[17] Zacher AH, Elliott DC, Olarte MV, Santosa DM, Preto F, Iisa K. Pyrolysis of woody residue feedstocks: upgrading of bio-oils from mountain-pine-beetle-killed trees and hog fuel. Energy Fuels 2014;28:7510–6.
[18] Zhao HY, Li D, Bui P, Oyama ST. Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on transition metal phosphide hydroprocessing catalysts. Appl Catal A 2011;391:305–10.
[19] S. Jones, C. Valkenburg, C. Walton, D. Elliott, J. Holladay, D. Stevens, C. Kinchin, S. Czernik, Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case, PNNL-18284, Rev. 1, Pacific Northwest National Laboratory: Richland, Washington, 2009.
[20] Arbogast S, Bellman D, Paynter JD, Wykowski J. Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities. Fuel Process Technol 2012;104:121–7.
[21] Speight JG. Handbook of Petroleum Product Analysis. Wiley; 2002.
[22] Robinson P. Petroleum Processing Overview. In: Hsu C, Robinson P, editors. Practical Advances in Petroleum Processing. New York, USA: Springer Science +Business Media Inc.; 2006.
[23] McCormick RL, Ratcliff MA, Christensen E, Fouts L, Luecke J, Chupka GM, et al. Properties of oxygenates found in upgraded biomass pyrolysis oil as components of spark and compression ignition engine fuels. Energy Fuels 2015;29:2453–61.
[24] Christensen ED, Chupka GM, Luecke J, Smurthwaite T, Alleman TL, Iisa K, et al. Analysis of oxygenated compounds in hydrotreated biomass fast pyrolysis oil distillate fractions. Energy Fuels 2011;25:5462–71.
[25] Baldwin RM, Feik CJ. Bio-oil stabilization and upgrading by hot gas filtration. Energy Fuels 2013;27:3224–38.
[26] Elliott DC, Wang H. Hydrocarbon liquid production via catalytic hydroprocessing of phenolic oils fractionated from fast pyrolysis of red oak and corn stover. ACS Sustainable Chem Eng 2015;3:892–902.
[27] Ferrell JR, Olarte MV, Christensen ED, Padmaperuma AB, Connatser RM, Stankovikj F, et al. Standardization of chemical analytical techniques for pyrolysis bio-oil: history, challenges, and current status of methods. Biofuels, Bioprod Biorefin 2016;10:496–507.
[28] Faix O, Andersons B, Zakis G. Determination of carbonyl groups of six round robin lignins by modified oximation and FTIR spectroscopy. Holzforschung 1998;52:268–74.
[29] Nicolaides GM. The chemical characterization of pyrolytic oils. Canada: Department of Chemical Engineering, University of Ontario; 1984.
[30] Wroblewski AE, Reinartz K, Verkade JG. Moisture determination of argonne premium coal extracts by P-31 NMR spectroscopy. Energy Fuels 1991;5:786–91.
[31] Wroblewski AE, Lensink C, Markuszewski R, Verkade JG. P-31 NMR spectroscopic analysis of coal pyrolysis condensates and extracts for heteroatom functionalities possessing labile hydrogen. Energy Fuels 1988;2:765–74.
[32] Argyropoulos DS. P-31 NMR in wood CHEMISTRY – a review of recent progress. Res Chem Intermed 1995;21:373–95.
[33] Granata A, Argyropoulos DS. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieities in lignins. J Agric Food Chem 1995;43:1538–44.
[34] Jiang ZH, Argyropoulos DS, Granata A. Correlation analysis of P-31 NMR chemical shifts with substituent effects of phenols. Magn Reson Chem 1995;33:375–82.
[35] Hu Z, Zheng Y, Yan F, Xiao B, Liu S. Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): Product distribution and bio-oil characterization. Energy 2013;52:119–25.
[36] Maddi B, Viamajala S, Varanasi S. Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass. Bioresour Technol 2011;102:11018–26.
[37] Diebold JP. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, NREL/SR-570-27613. Golden, Colorado: National Renewable Energy Laboratory; 2000.
[38] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils – state of the art for the end users. Energy Fuels 1999;13:914–21.
[39] Song C, Ma X. Ultra-Clean Diesel Fuels by Deep Desulfurization and Deep Dearomatization of Middle Distillates. In: Hsu C, Robinson P, editors. Practical Advances in Petroleum Processing. New York, USA: Springer Science+Business Media Inc.; 2006.
[40] EPA, FRL-3856-9: Regulation of Fuels and Fuel Additives; Definition of Substantially Similar, 1990.
[41] Christensen E, Yanowitz J, Ratcliff M, McCormick RL. Renewable oxygenate blending effects on gasoline properties. Energy Fuels 2011;25:4723–33.
[42] L. Gibbs, B. Anderson, K. Barnes, G. Engeler, J. Freel, J. Horn, M. Ingham, D. Kohler, D. Lesnini, R. MacArthur, M. Mortier, D. Peyla, B. Taniguchi, A. Tiedemann, S. Welstand, D. Bernhardt, K. Collini, A. Farr, J. Jones, J. Lind, C. Tom, J. Benson, Motor Gasolines Technical Review, Chevron Corporation, 2009.
[43] Jones DM, Watson JS, Meredith W, Chen M, Bennett B. Determination of naphthenic acids in crude oils using nonaqueous ion exchange solid-phase extraction. Anal Chem 2001;73:703–7.
[44] Christensen E, Alleman T, McCormick R. Total acid value titration of hydrotreated biomass fast pyrolysis oil: determination of carboxylic acids and phenolics with multiple end point detection. Abstr Pap Am Chem Soc 2013;245.
[45] Black S, Ferrell III JR. Determination of carbonyl groups in pyrolysis bio-oils using potentiometric titration: review and comparison of methods. Energy & Fuels 2016;30:1071–7.
[46] Lissitsyna K, Huertas S, Quintero LC, Polo LM. PIONA analysis of kerosene by comprehensive two-dimensional gas chromatography coupled to time of flight mass spectrometry. Fuel 2014;116:716–22.
[47] Routray K, Barnett KJ, Huber GW. Hydrodeoxygenation of pyrolysis oils. Energy Technol 2017;5:80–93.

Please cite this article in press as: Olarte MV et al. Characterization of upgraded fast pyrolysis oak oil distillate fractions from sulfided and non-sulfided catalytic hydrotreating. Fuel (2017), http://dx.doi.org/10.1016/j.fuel.2017.03.051