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Production of low-oxygen bio-oil via ex situ catalytic fast pyrolysis and hydrotreating

Kristiina Iisa*, Richard J. French, Kellene A. Orton, Abhijit Dutta, Joshua A. Schaidle

National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA

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ABSTRACT

Catalytic fast pyrolysis (CFP) bio-oils with different organic oxygen contents (4–18 wt%) were prepared in a bench-scale dual fluidized bed reactor system by ex situ CFP of southern pine over HZSM-5, and the oils were subsequently hydrotreated over a sulfided CoMo catalyst at 170 bar. The goal was to determine the impact of the CFP oil oxygen content on hydrotreating requirements. The CFP oils with higher oxygen contents included a variety of oxygenates (phenols, methoxyphenols, carbonyls, anhydrosugars) whereas oxygenates in the 4 wt% oxygen oil were almost exclusively phenols. Phenols were the most recalcitrant oxygenates during hydrotreating as well, and the hydrotreated oils consisted mainly of aromatic and partially saturated ring hydrocarbons. The temperature required to produce oil with <1% oxygen was approximately 350 °C for the CFP oil with the lowest oxygen content whereas temperatures around 400 °C were required for the other CFP oils. The carbon efficiency during hydrotreating slightly decreased as the CFP oil oxygen content increased but remained above 90% in all cases, and the carbon efficiency for the integrated process was dominated by the efficiency of the CFP process. A preliminary technoeconomic evaluation suggested that with the current zeolite-based CFP catalysts, it is economically beneficial to preserve carbon during CFP, at the expense of higher oxygen contents in the CFP oil.

1. Introduction

Biomass can be converted to a liquid with high yields via fast pyrolysis (FP), which involves rapid heating of biomass to temperatures of 500–600 °C in the absence of oxygen for times of less than 2 s [1–3]. The product oil (FP oil or bio-oil) has elemental composition similar to the original biomass and consists of hundreds of oxygenated compounds, including anhydrosugars, acids, aldehydes, ketones, phenolic compounds, and lignin-derived oligomers. Pyrolysis oil has a low heating value compared to fossil fuels because of the presence of water and oxygenates, is acidic (pH ~2), leaves a high residue during heating (~50%), and undergoes reactions during storage; thus, it needs to be upgraded for use as a transportation fuel. One method of upgrading is catalytic fast pyrolysis (CFP), in which biomass pyrolysis vapors are upgraded over a catalyst prior to their condensation to produce partially deoxygenated, stabilized oils. The upgrading catalyst may be placed in the pyrolysis reactor (in situ CFP) or in a separate reactor through which pyrolysis vapors are passed prior to condensation (ex situ CFP or vapor phase upgrading). Zeolites, in particular HZM-5, have been the catalysts of choice due to their ability to deoxygenate pyrolysis vapors by a combination of dehydration, decarbonylation, decarboxylation, cracking, isomerization, cyclization and aromatization reactions [4–10]. The properties of CFP oils vary widely based on catalyst used and operating conditions. Mukarakate et al. [11] compiled data from several studies for CFP over HZSM-5 and showed that the CFP oil oxygen content and oil yield could be correlated to the ratio of biomass to catalyst. At low biomass-to-catalyst ratios, when the catalyst is fresh, mainly aromatic hydrocarbons are formed. As the biomass-to-catalyst ratio is increased, the catalyst becomes deactivated and oxygenates are progressively formed.

For cost-competitive production of biofuels it is important to obtain high yields of the CFP oil and the final biofuel product. Low product yields may have been largely responsible for the recent failure of commercial-scale production of biofuels via CFP. The fraction of biomass carbon converted to CFP oil – oil carbon yield - increases as less deoxygenated oil (i.e., oil with higher oxygen content) is produced. Data on CFP of biomass over HZSM-5 have been compiled in Table 1. For oils with low oxygen contents, carbon yields of 4–15% have been reported[12–14] whereas for oils with approximately 20% oxygen on dry basis, typical reported carbon yields are 21–28% though values as high as 32% have been related [15].

CFP oils have improved properties compared to FP oil; they have reduced contents of anhydrosugars, carbonyls, and acids and also lower water contents than FP oils because of the formation of a separate aqueous phase [13,18,20,22,24,26]. However, CFP oils still contain significant amounts of organic oxygen and are unsuitable for use

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* Corresponding author.
Email address: kristiina.iisa@nrel.gov (K. Iisa)

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Table 1
Data on oil carbon yield and oil oxygen content for CFP of biomass over HZSM-5. Experiments in fluidized bed unless otherwise indicated.

Feedstock	Upgrading Temp., °C	Mode	Biomass Feed, kg/h	Oil Yield, g/g feed	Oil C Yield, g C/g C	Oil O, wt% dry basis	Ref.
Pine	550	in situ	0.03	NR	15%	NR (low)	[16]
Pine	600	in situ	0.03	NR	12%	NR (low)	[16]
Pine	600	in situ	NR(~0.03)	NR	14%	NR (low)	[12]
Pine	600	in situ	NR(~0.1)	NR	15%	NR (low)	[13]
Hybrid poplar	500	in situ	0.1	18–21%	10%	22%	[17]
Hybrid poplar	425–450	ex situ	NR	12%	NR	10–18%	[18]
Lignocell HBS	400	in situ	0.1–1.8	31%	NR	NR (high)	[19]
Lignocell HBS	400	in situ	0.1–1.9	44%	NR	NR (high)	[19]
Lignocell HBS	400	in situ	0.1–1.10	36%	NR	NR (high)	[19]
Beechwood	500	ex situ*	0.0015 (batch)	6%	NR	4%	[14]
Beechwood	500	ex situ*	0.0015 (batch)	21%	NR	31%	[14]
Beechwood	500	in situ	NR (~0.5)	25%	NR	14%	[20]
Beechwood	482	in situ	~1	23%	32%**	18%	[15]
Corncob	550	in situ	~0.04	14%	NR	15%	[21]
Pine	500	in situ	0.15	17%	25%	18%	[22]
Pine	500	ex situ	0.15	14%	21%	16%	[22]
Pine	500	ex situ	0.15	15%	23%	20%	[23]
Pine	500	ex situ	0.15	16%	23%	22%	[23]
Pine	520	in situ	20	32%	24%	22%	[24]
Beechwood	500	in situ	0.5	18%	27%	20%	[25]
Beechwood	500	in situ	0.5	18%	28%	18%	[25]
Beechwood	500	in situ	0.5	17%	27%	19%	[25]
Beechwood	500	in situ	0.5	15%	24%	18%	[25]

NR Data not reported.

* Fixed bed of catalyst, batch of biomass.

** Calculated from data in reference.

as finished transportation fuels. The final deoxygenation needs to be accomplished by hydroprocessing [27,28]. Hydroprocessing is well known for petroleum processes and has been studied for FP oils for decades [29–34]. Two to three stages of hydrotreating, at increasing severity, are required for upgrading FP oil to prevent coking by olefins, aldehydes, ketones, and sugars [29,30,35,36]. Traditional hydrotreating catalysts, sulfided nickel-molybdenum (NiMo) and cobalt molybdenum (CoMo) on alumina supports, and precious metal catalysts on carbon supports have been the materials of choice for pyrolysis oil hydrotreating [29,37–39]. Precious metals are typically more active than the sulfided Mo-based catalysts but lead to higher hydrogen consumption [38,40]. Consequently, precious metals, in particular Ru/C, have been used for the initial oil stabilization stage and the first hydrotreating stage at temperatures of 140–200 °C [35,41,42]. For the final stage operating at around 400 °C both sulfided Mo-based catalysts and precious metal catalysts have been evaluated [36,41–43]. Sulfided CoMoS was shown to be effective for deoxygenation of the phenolic fraction of pyrolysis oil [44].

CFP oils differ from both petroleum fractions and FP bio-oils, and thus the conditions required for obtaining finished fuels from FP and CFP oils via hydrotreating are likely to be different. Limited information on hydrotreating of CFP oils is available. Due to the reduced contents of reactive species, it may be possible to hydrotreat CFP oils in one stage. CFP oil prepared from pinyon juniper over red mud was successfully hydrotreated in a single step over a sulfided CoMo on zirconia catalyst at 400 °C [28]. The reactor was operated over 300 h without signs of cross-linked polymer or carbonaceous particulate deposits. The oil yields were considerably higher than reported for FP oils in a typical two-stage process: 72–76% vs. 40–45%. Hydrogen consumption was 0.07 g H_2/g oil. In another study, CFP oil from pine with 19.5 wt% oxygen was hydrotreated over a sulfided catalyst at 290-350 °C and 100–138 bar [45]. The catalyst exhibited deactivation and the product oxygen contents ranged from 0.08 to 11 wt%. Hydrogen consumption was 0.04–0.07 g H_2/g oil and average carbon efficiencies were 77–89%.

For an overall efficient and economic process, catalytic fast pyrolysis and hydrotreating need to be optimized together. High severity during CFP produces oil with low oxygen content but at low yield; conversely, low severity during CFP results in a higher yield of oil with higher oxygen content but the oil may require higher severity during hydrotreating and/or consume more hydrogen. The objective of the current work was to evaluate the impact of CFP oil oxygen content on hydrotreating. Three CFP oils with different oxygen contents were prepared in a bench-scale fluidized bed reactor system. HZSM-5 was the chosen catalyst because of the large amount of information available for this material. The oils were hydrotreated over sulfided CoMo/Al_2O_3 at different temperatures with the goal to produce oil suitable for blending with petroleum fuels. Sulfided CoMo was selected as the catalyst because of its wide use in the refinery industry and in the final stage of hydrotreating of FP oils [41–43]. Further, phenols are important compounds in catalytic pyrolysis oil produced over HZSM-5 [22] and sulfided CoMo has exhibited high deoxygenation of phenolic compounds [44]. An acceptable upper limit on organic oxygen content for finished fuels has not been established by the petroleum refining industry and likely depends on the oxygenated species present. 1 wt% oxygen was selected as the oxygen content target for hydrotreating in a recent design report [27] and the same target was adopted here. The optimization of the combined process of CFP and hydrotreating is discussed and a preliminary technoeconomic evaluation is presented based on the findings of the research.

2. Experimental

2.1. Materials

The biomass feedstock for the CFP oil production was southern yellow pine, provided by Idaho National Laboratory and knife-milled to a particle size of <0.5 mm. The biomass elemental composition on wet basis was 49.6 wt% C, 6.3 wt% H, 43.5 wt% O, 0.1 wt% N, <0.1 wt% S, and 0.3 wt% ash, and the water content was 2.3%.

The catalyst for CFP was HZSM-5 with a silica-to-alumina ratio of 30 from Nexceris (Lewis Center, OH). The catalyst was prepared by spray drying; it contained 20 wt% SiO_2 as a binder and was sieved to a nominal particle size of 300–1000 μm. The catalyst possessed an acid site concentration of 960 μmol/g as determined by temperature-programmed NH_3 desorption [23], and the BET surface area was 370 m^2/g.

The hydrotreating catalyst was based on CoMo on γ-alumina support from Alfa Aesar (Product # 45579) and, per the manufacturer, it contains 4% cobalt oxide and 11.5–14.5% molybdenum oxide. The catalyst sulfidation was performed by Wil Swanson & Associates (Golden, CO). The catalyst was heated at a rate of 30 °C/min from room temperature to 390 °C in a flow of 5% H_2S/95%H_2, held at 390 °C for 2 h and then cooled in the same gas atmosphere. The sulfided catalyst was packaged and stored under inert gas. It had a BET surface area of 300 m^2/g, and the median particle size was determined to be <100 μm by automated image analysis as described in [46].

2.2. Catalytic fast pyrolysis experiments

Three CFP oils were produced in a bench-scale fluidized bed reactor system, which is described in detail elsewhere [22]. The system consists of two bubbling fluidized bed reactors with inner diameters of 5.2 cm: a pyrolysis reactor with quartz sand as bed material and an upgrading reactor in which 140 g of the HZSM-5 catalyst was placed. After the pyrolyzer, the vapors were passed via a cyclone to the upgrading reactor. The upgraded vapors from the second reactor passed through a 2-μm stainless-steel mesh hot gas filter to the condensation train, which consisted of an air-cooled condenser, an electrostatic precipitator, a dry-ice trap, and a coalescing filter. Both the pyrolysis and upgrading reactor were maintained at 500 °C. During CFP experiments, pine was continually fed into the pyrolyzer at a rate of 150 g/h, which gave a weight hourly space velocity (WHSV) of approximately 1 h^{-1} for the upgrading. Fast pyrolysis (FP) oil was produced as a comparison in the same system with the second reactor by-passed and with a feed rate of 420 g/h. A lower feed rate was used for the CFP experiments to provide better control of the amount of biomass fed and provide a lower WHSV.

The CFP experiments were conducted as a series of catalytic and regeneration cycles. The ratio of the mass of biomass fed in one cycle to the mass of catalyst in the upgrading reactor - the biomass-to-catalyst ratio (B:C) – was kept constant in each experiment. When the predetermined B:C ratio (2.1, 1.5, or 0.5 g biomass/g catalyst) was reached, biomass feed was stopped and the catalyst was regenerated by oxidation at 550 °C in a mixture of air and N_2 to remove coke. A low regeneration temperature was selected to prevent changes to the HZSM-5 crystal structure. The regeneration was monitored by measuring the CO and CO_2 contents in the exit gas. After the catalyst was regenerated, a new catalytic cycle was initiated. The number of catalytic cycles was determined by the need to produce a minimum of 150 g oil for the hydrotreating experiments and varied from 6 cycles for the highest B:C ratio to 35 cycles for the lowest B:C ratio.

The total liquid yield was determined from the weight change in the condensation train. After the experiments, the liquids from the receivers were combined and allowed to phase-separate, and the mass of each phase was weighed. Gas formation during the catalytic cycles was determined from the analysis of H_2, CO, CO_2, and C_1- C_4 hydrocarbons by a Varian micro-GC with Molecular Sieve 5A, Porabond Q, and CP-Sil columns and measurement of the dry gas flow rate. The char yield was calculated from the weight change in the cyclone and the pyrolysis reactor bed. The total amount of coke formed was determined from the CO and CO_2 produced during catalyst regeneration and thermogravimetric analysis of the spent catalyst from the last cycle.

2.3. Hydrotreating experiments

The CFP oils were hydrotreated in a 100-ml Parr reactor connected to a He cylinder and a 500-ml transportation cylinder filled with high-pressure H_2. 30 ± 0.15 g of oil (approximately 25 ml) and 3.0 ± 0.1 g of the sulfided CoMo catalyst were placed in the reactor vessel inside a glove bag, which was operated so as to have <50 ppm O_2 to prevent catalyst oxidation. The reactor vessel was attached to the Parr reactor assembly, leak tested with He, and filled with 90 bar H_2. 3.4 bar He was added as an internal standard. The reactor was heated at a rate of ∼15 °C/min to the hydrotreating temperature and held at that temperature for 3 h. At the final temperature, the total pressure was maintained at 170 bar by adding hydrogen from the transportation cylinder. The hydrogen partial pressure was lower than the total pressure due to light gases released and vaporization of water and other light compounds from the oil. Based on product gas analysis, the hydrogen partial pressure varied between 120 and 145 bar at the end of the experiments.

Due to the high water content of the FP oil, a modified procedure was adopted. The water vaporizes at the hydrotreating conditions, and the water partial pressure would have been in excess of 240 bar if 25 ml of the FP oil had been used and this would have prevented inclusion of hydrogen in the reactor. Therefore, the amount of FP oil was reduced to 6.4 g, and dodecane was added to fill the reactor to 25 ml. This procedure resulted in water and hydrogen partial pressures commensurate with the CFP oil experiments.

After hydrotreating, the reactor was allowed to cool and the gas from the reactor was collected in a 25-L gas bag. The reactor contents were filtered to separate the liquid product and the catalyst solids. A separate aqueous phase (<0.1 g) was detected in some oils, but not in all. The reactor and the solids were rinsed with 25 ml of pyridine to collect any residual liquid and the reactor head space and the solids were further rinsed with 25 ml of acetone to remove any residues.

All CFP oils were hydrotreated at 360 and 390 °C. The most deoxygenated CFP oil was also hydrotreated at a lower temperature (330 °C) and the least deoxygenated oil at a higher temperature (420 °C). One experiment (B:C 1.5 oil at 360 °C) was performed in duplicate.

The gas bag samples from the hydrotreating experiments were analyzed by the CFP reactor micro-GC for He, H_2, CO, CO_2, and C_1-C_4 hydrocarbons, and light gas formation was calculated from the gas composition and the gas volume. Coke formation was determined based on the inorganic residue content of the solids before and after the experiments. The liquid yields in the hydrotreating experiments were calculated as the difference between the mass of reactor contents after the experiments and the solids (catalyst and coke) mass. The amount of hydrogen consumed was determined from the pressure change in the H_2 transportation cylinders and from the amount of H_2 remaining in the reactor after the experiment. The hydrogen consumed for deoxygenation was calculated from the changes in oil oxygen content taking into account oxygen removed as CO or CO_2, and hydrogen consumed for oil hydrogenation was calculated from the change in oil hydrogen content.

2.4. Chemical analysis

The CFP oils, FP oil, hydrotreated oils, feedstock, and the fresh and spent catalysts were analyzed for ultimate composition (C, H, N, S, direct O, ash) at Huffman Hazen Laboratories (Golden, CO). The oils were analyzed for water content by Karl Fisher titration, carboxylic acids by potentiometric titration with NaOH [47], and carbonyls by a modified Zakas/Faix method [48]. The composition of the oils was further analyzed by gas chromatography – mass spectrometry (GCMS) and ^{13}C nuclear magnetic resonance (NMR) by methods described in [49] and [50]. More details on the analytical methods are available in the Supplementary Information.

2.5. Preliminary technoeconomic analysis

The CFP and hydrotreating results were used to arrive at relative Minimum Fuel Selling Prices (MFSP) using Aspen Plus software and assumptions in the ex situ CFP process documented by Dutta et al. [27]. To obtain closed mass and carbon balances, any missing material was allocated proportionally among the different phases (char, coke, organic oil, aqueous liquid, and gases). This normalization was done only for the technoeconomic calculations, and all other results are presented on non-normalized basis.

3. Results and discussion

3.1. Catalytic fast pyrolysis

The mass yields of the products in the pyrolysis experiments are shown in Table 2. During FP, only one liquid phase was formed, whereas three liquid phases were obtained in all CFP experiments: top organic layer, middle aqueous layer, and bottom organic layer. The bottom organic layer constituted the majority of the organic liquid (>90% for the B:C 2.1 and 1.5 experiments and 73% for the B:C 0.5 experiment). The yields of the two organic phases are combined in the oil yield. Compared to FP, CFP produced lower total liquid yields and higher gas and solids yields as well documented in the literature, e.g. [5,18]. The water content of the FP oil was higher than that of the CFP oils (18 wt% vs. 3–5 wt%). However, a separate aqueous phase was formed during CFP and, overall, more water was produced during CFP than FP.

Table 2
Mass yields of products and oil analysis for fast pyrolysis and catalytic pyrolysis.

B:C, g/g	0.5	1.5	2.1	FP/No cat
Yields, wt%				
Oil	8.1	10.9	15.3	72.7
Aqueous	23.9	21.9	24.1	–
Light gases	34.2	32.5	31.2	12.3
Condensable vapors[a]	na	na	4.9	na
Water vapor[b]	3.2	3.2	3.2	1.1
Char	10.3	10.0	10.5	9.2
Coke	9.1	6.4	4.8	–
Total	88.8[c]	84.9[c]	94.0	95.3
Light gas yields, wt%				
H_2	0.1	0.1	0.1	0.1
CH_4	0.8	0.8	1.0	0.5
CO	16.9	16.9	16.5	5.5
CO_2	12.1	10.7	10.0	5.7
C_2-C_4 olefins	4.4	4.1	3.6	0.4
Oil analysis				
C, wt% dry basis	87.9	78.4	75.1	59.0
H, wt% dry basis	8.0	7.3	7.1	6.8
O, wt% dry basis	4.0	14.2	17.7	33.8
N, wt% dry basis	0.1	0.1	0.1	0.1
H_2O, wt%	5.5	4.2	3.2	18.0
Acid, mg KOH/g	0.0	15.9	24.5	76.1
Carbonyls, mol/kg	0.5	5.5	2.1	5.7

[a] Condensables from GCMS analysis of gas bag samples; na = not analyzed.

[b] Water vapor estimated by water vapor pressure at 0 °C, the coalescing filter temperature.

[c] Does not include condensables.

CFP produces low-molecular weight compounds that have relatively low boiling points and are difficult to capture in the condensation system of a bench-scale system such as used here. In one CFP experiment (B:C 2.1), vapor products were measured and quantified by GCMS analysis of exit gas samples. The analysis showed furans (furan and methylfuran), carbonyls (acetone, butenone), and light hydrocarbons (cyclopentadiene, benzene, and traces of toluene), in quantities corresponding to approximately 5% of the biomass feed or 7% of the carbon in the biomass. In commercial scale systems, the majority of these compounds would be captured and they would increase the CFP oil yield. Similarly, most of the water vapor reported in Table 2 would also be condensed and included in the aqueous yield. The loss of vapors was accentuated in the CFP experiments because of the lower biomass feed rate, which reduced the vapor concentrations.

The yields of carbon (g C in product/g C in feed) in the main products together with the oil oxygen contents are illustrated in Fig. 1 for the CFP experiments. The carbon yields were calculated from the measured, non-normalized yields of each product and the carbon contents of the product and the feed. The oil oxygen content and the oil yield increased as the B:C ratio was increased, in accordance with previous studies as summarized in [11]. The oil carbon yields also agree with those measured in other studies (see Table 1) with 14% carbon yield for the oil with the lowest oxygen content and 23% carbon yield for oil with 18% oxygen. The increase in oil carbon yield was accompanied by a decrease in gas and coke carbon yields and an increase in the aqueous carbon yield. As the vapors retain more oxygen, the solubility of the product molecules in the aqueous phase rises; this increases the loss of carbon into the aqueous phase. However, the carbon loss in the aqueous phase always remained low (<5%).

The gas yields of various compounds are included in Table 2. Compared to FP, CFP produced 2–3 times higher yields of CO and CO_2, and ten times higher yields of C_2-C_4 olefins. The increase was larger for CO than for CO_2, suggesting that the catalyst favored decarbonylation over decarboxylation. Decarboxylation could conceivably take place from acids or esters, but is not as likely from other oxygenate groups and, therefore, CO_2 production may be limited. Within the CFP experiments, CO_2 yields decreased slightly as the B:C ratio increased whereas CO yields remained relatively constant. This suggests that the decarboxylation activity of the HZSM-5 catalyst decreased as the catalyst became deactivated in the range studied, but the decarbonylation activity remained relatively constant.

The composition of the oils is summarized in Table 2. The organic oxygen contents of the CFP oils were significantly reduced compared

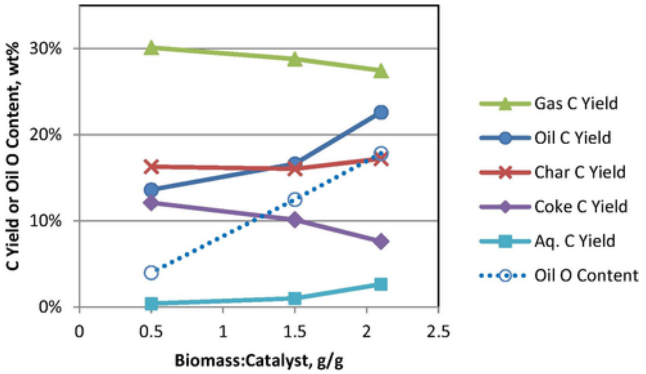

Fig. 1. Oil oxygen content on dry basis and yields of carbon (g C/g C in feed) in oil, gas, coke, and the aqueous liquid.

to the FP oil. The oil produced in the B:C 0.5 experiment had only 4 wt% oxygen on a dry basis, and the oil produced in the B:C 2.1 experiment had 18 wt% oxygen. Of the oxygen in biomass, only 1–10% remained in the CFP oils; 40–45% was removed as CO and CO_2, small fractions remained in solids (<10%), and the remainder (approximately 45%) was removed as H_2O. The carboxylic acids and carbonyls were also lower in the CFP than in the FP oil, and no carboxylic acids were detected in the oil with the lowest B:C ratio. The increase in acid content as B:C increased is consistent with the decrease in CO_2 formation. Even though the carboxylic acid concentration in the CFP oil with the highest B:C is similar to that in the FP oil, the amount of acid from CFP is still significantly lower due to the much lower CFP oil yield.

A summary of the compounds identified by GCMS analysis of the oils is shown in Fig. 2a. Only oxygenates were detected in the FP oil and they included methoxyphenols, phenols, acids, carbonyls, and anhydrosugars (levoglucosan) as the major compound groups. In contrast, aromatic hydrocarbons constituted the majority of the compounds detected by GCMS in all of the CFP oils, with 2-ring compounds as the largest aromatic group. The oxygenates in the B:C 2.1 and 1.5 oils included compounds with hydroxyl groups (phenols, indenols, and naphthols) and with methoxy groups (methoxyphenols) as well as carbonyls, levoglucosan, and furans. No levoglucosan or methoxyphenols were detected in the B:C 0.5 oil. Thus, the B:C 0.5 oil not only had a lower oxygen content, but it had fewer types of oxygen functional groups than the other two CFP oils.

The results of the ^{13}C NMR analysis (Fig. 2b) are in good agreement with the GCMS analysis. In the CFP oils, aromatic C–H and C–C bonds constituted the majority, consistent with the high aromatic hydrocarbon content by GCMS analysis. In the FP oil, aromatic C–H and C–C represent aromatic rings in methoxyphenols. Aliphatic C–C bonds, which were present in all oils at similar levels, include those in the side chains of e.g. aromatics. For the FP oil, the largest oxygen functional group was aliphatic C-O, which includes, for example, anhydrosugars. The aliphatic C-O content was over 75% reduced in all CFP oils and non-existent in the B:C 0.5 oil. Other functional groups, which were significantly reduced in the CFP oils, were C=O (acids, aldehydes, and ketones) and methoxy groups. The reduction in C=O is in particular of interest since carbonyls are deemed largely responsible for the instability of FP oils during hydrotreating [35,36,51]. This may eliminate the need for prestabilization prior to hydrotreating. Aromatic C-O carbons, which include those in phenols and furans, remained in all CFP oils, indicating the recalcitrance of these types of carbon–oxygen bonds. – The ^{13}C NMR analysis characterizes all carbons in the oils whereas the GCMS analysis only identifies the fraction that vaporizes in the GC. The fact that the two analyses show similar distributions of functional groups suggests that the compounds not detected by GCMS are similar to those detected.

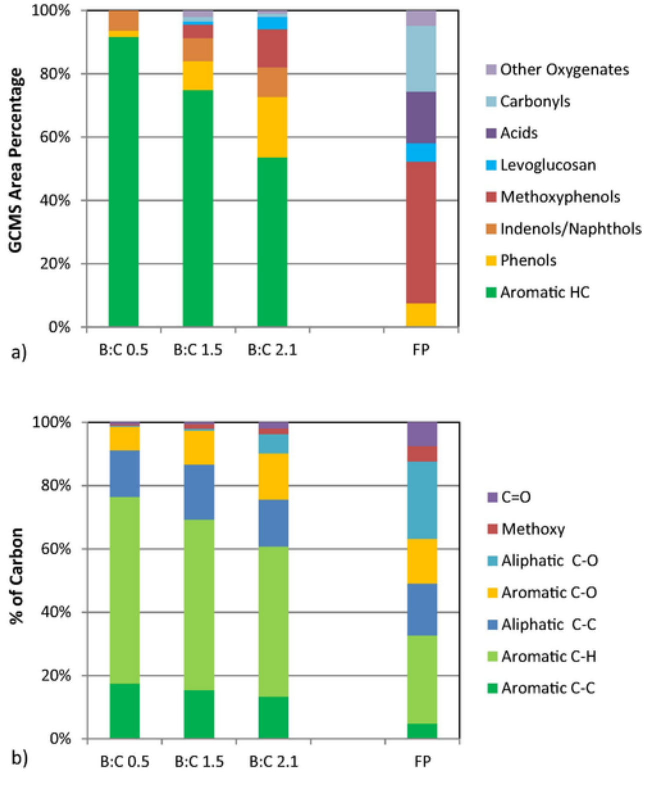

Fig. 2. a) GCMS analysis and b) ^{13}C NMR analysis of the FP and CFP bottom oils. The CFP oils are identified by the biomass-to-catalyst mass ratio (B:C) in the experiments. The other oxygenates in GCMS analysis included furans and alcohols.

Overall the CFP results show that the oil oxygen content can be varied by changing the biomass-to-catalyst ratio and that oils with very low organic oxygen contents can be produced, but at low yields. The CFP oils with 14–18% organic oxygen contained a variety of oxygenated compounds (phenols, methoxyphenols, carbonyls, anhydrosugars, and acids) whereas the oxygenates in the 4% oxygen oil were almost exclusively phenols.

3.2. Hydrotreating

The yields of liquids, gases, and coke during hydrotreating are given in Table 3. In one of the experiments (B:C 2.1 oil at 360 °C), oil splashed out of the reactor when the gas bag was filled, but for all other experiments, the sums of the product yields were 97–102% based on the CFP oil input. The total balance is expected to exceed 100% due to incorporation of hydrogen. The liquid yields were higher and gas and coke yields lower for the CFP oils than for the FP oil. In general, the liquid yields decreased and gas yields increased as the CFP oil oxygen content increased. The organic oxygen contents in the hydrotreated CFP oils varied from 0.5 wt% to 4 wt%. No acid and only low levels of carbonyls were detected by the titration methods in any of the hydrotreated CFP oils. The CFP oil with 18 wt% oxygen was also hydrotreated at 420 °C but a large amount of solids was formed, and the results are not included. The composition of the hydrotreated FP oil could not be reliably calculated due to the dilution with dodecane and the results are not included.

The yields of light gases are also shown in Table 3. CO_2 was the main gas component and the CO_2 formation roughly correlated with the acid content of the CFP oils; for example, the CO_2 yield corresponding to the acid detected in the B:C 2.1 oil is 5.5% and the measured CO_2 yield at the highest hydrotreating temperature was 5.4%. The low CO formation for all CFP oils is due to the fact that most of the functional groups that undergo decarbonylation were removed during CFP. Oxygen in the remaining phenols is removed as H_2O. Other light gases detected included CH_4 (likely from methoxy groups) and C_2-C_4 alkanes (likely from side chains in lignin derivatives). The trends in light gas formation during CFP and hydrotreating are opposite: deoxygenating to a greater extent during CFP increases light gas formation during CFP (Table 2 and Fig. 1) but reduces light gas formation during hydrotreating (Table 3). During hydrotreating, the difference between the gas yields for the B:C 2.1 oil and B:C 0.5 oil was 0.05–0.07 g gas/g CFP oil. Taking into account the yields of CFP oils, these values translate to approximately 0.01 g gas/g biomass, which is smaller than the difference in gas

Table 3
Mass yields of liquids, gas, and coke in the hydrotreating experiments.

CFP Oil										
CFP OIl B:C, g/g	0.5			1.5			2.1		FP	
Oil O, wt%	4.0			14.2			17.7		33.9	
Hydrotreating Temp., °C	330	360	390	360	360	390	360	390	360	390
Yields, g/g CFP oil										
Liquid	97.3%	95.2%	96.2%	95.3%	95.4%	94.6%	81.9%[a]	91.2%	77.7%	73.0%
Gases	1.2%	1.2%	1.8%	4.4%	3.7%	5.7%	6.7%	9.3%	19.3%	20.9%
Coke	1.1%	1.9%	1.6%	1.3%	1.7%	1.4%	1.7%	1.7%	2.9%	3.6%
Total	99.5%	98.3%	99.6%	101.0%	100.8%	101.7%	90.3%[a]	102.2%	99.9%	97.6%
Light Gas Yields, wt%										
CH_4	0.6%	0.4%	0.7%	1.6%	1.3%	1.7%	1.6%	2.0%	2.4%	2.9%
CO	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.9%	0.0%	0.7%	0.6%
CO_2	0.4%	0.6%	0.8%	2.2%	1.9%	3.0%	3.4%	5.4%	12.7%	13.0%
C_2-C_4 Alkanes	0.1%	0.1%	0.3%	0.3%	0.5%	1.0%	0.8%	1.9%	3.6%	4.3%
Oil Analysis										
C, wt% (db)[b]	89.3%	90.8%	90.6%	89.2%	89.1%	90.3%	87.1%	83.8%	NA[c]	NA
H, wt% (db)	8.9%	8.9%	8.7%	9.0%	9.1%	9.1%	8.6%	8.2%	NA	NA
O, wt% (db)	1.4%	0.8%	0.5%	2.3%	2.2%	1.3%	4.1%	3.4%	NA	NA
N, wt% (db)	0.0%	0.0%	0.0%	0.1%	0.1%	0.1%	0.2%	0.1%	NA	NA
H_2O, wt%	0.1%	0.1%	0.0%	0.3%	0.2%	0.3%	2.7%	0.5%	NA	NA
Acid, mg KOH/g	<2	<2	<2	<2	<2	<2	<2	<2	NA	NA
Carbonyls, mol/kg	<0.1	<0.1	0.1	0.1	0.1	0.1	0.2	0.2	NA	NA

[a] Oil was lost when the gas bag was filled and hence the oil yield is low.

[b] db = dry basis.

[c] NA = Not analyzed/calculated because oil was diluted in dodecane.

yields during CFP, which was approximately 0.03 g gas/g biomass. Thus, deoxygenation during hydrotreating produces less light gases than deoxygenation during CFP. This is due to the hydrogen available under hydrotreating conditions, which facilitates hydrodeoxygenation instead of decarbonylation and decarboxylation. The oxygen contents in the hydrotreated CFP oils are presented as a function of the hydrotreating temperature in Fig. 3a. Increasing the hydrotreating temperature enhanced deoxygenation as evidenced by the decreasing oil oxygen contents. With the B:C 0.5 oil, it was possible to reduce the oil oxygen content to below 1 wt% at 360 °C. For the other two CFP oils, temperatures in excess of 390 °C would be required to reach 1 wt% oxygen at the conditions of these experiments.

Hydrodeoxygenation was the main method of oxygen removal during hydrotreating as illustrated in Fig. 3b, which shows the fate of organic oxygen for the CFP oils hydrotreated at 360 and 390 °C. 8–18% of the organic oxygen remained in the product oil, 12–25% was removed as gases, and the remainder, 62–75%, was removed as water. Compared to CFP, a higher fraction of the organic oxygen was removed as water during hydrotreating.

A summary of the GCMS analysis of the hydrotreated CFP oils is presented in Fig. 4a. The majority of the hydrocarbons retained their aromaticity, but some ring hydrogenation was observed. The conversion of one-ring aromatics to cyclohexanes was low, and the hydrogenated multi-ring compounds typically retained at least one aromatic ring and included indanes, tetrahydronaphthalenes (tetralins), and di-, tetra-, and octahydrophenanthrenes or –anthracenes. Ring hydrogenation becomes thermodynamically limited at higher temperatures, which is reflected in the lower fractions of saturated compounds at 390 °C than at 360 °C. Phenols were the predominant oxygenates, consistent with their recalcitrant nature [29]. The other oxygenates included dibenzofurans, which also require high temperatures for deoxygenation. The fraction of oxygenates was lower for the CFP oils with lower initial oxygen contents and, for each CFP oil, the oxygenate fraction decreased as the hydrotreating temperature increased.

The ^{13}C NMR analysis, shown in Fig. 4b, confirms that the remaining oxygenates were mainly phenolic components (carbons with aromatic C-O bonds). Traces of methoxy and carbonyl groups were detected in the products from hydrotreating at 360 °C and from the B:C 2.1 oil also at 390 °C. The NMR analysis also shows that the majority of the carbon remained aromatic. Compared to the analysis of the starting materials (Fig. 2b), the fraction of aliphatic C–C carbon had increased, consistent with hydrogenation of aromatic rings. The aliphatic C–C decreased as the hydrotreating temperature increased, as a result of lower aromatic bond saturation at higher temperatures, as was also observed by the GCMS analysis.

A van Krevelen diagram for the CFP oils and the hydrotreated CFP oils is shown in Fig. 5. Increasing the B:C ratio during pyrolysis increased both O:C and H:C ratios. The oxygenated compounds formed over a deactivated CFP catalyst have higher hydrogen contents than the fully deoxygenated CFP products, which increases the H:C ratios. Hydrotreating reduced oxygen contents and increased hydrogen contents for all oils. Oils hydrotreated at 390 °C had lower oxygen contents, but also slightly lower H:C ratios than the oils hydrotreated at 360 °C, consistent with the aromatic rings being less hydrogenated at the higher temperature. The hydrotreated oils resembled each other more closely than the original CFP oils indicating that, regardless of the severity of CFP process, similar oils were produced during hydrotreating.

The hydrogen consumption is illustrated in Fig. 3c. Hydrogen consumption was lowest for the B:C 0.5 oil and similar for the B:C 1.5 and 2.1 oils. The hydrogen consumption for the B:C 1.5 and 2.1 oils (0.04–0.05 g/g CFP oil) was in good agreement with the previous studies of CFP oil hydrotreating [28,45]. For all oils, hydrogen consumption decreased as the hydrotreating temperature increased reflecting the reduced aromatic ring saturation identified by oil analysis. Fig. 3d shows separately the hydrogen consumed for deoxygenation and hydrogenation of the oils. The hydrogen consumed for deoxygenation was higher for oils produced at higher B:C ratios due to their higher initial oxygen contents. Hydrogen consumed for hydrogenation surpassed that for deoxygenation for the CFP oils with the lower oxygen contents. Overall, the significantly lower hydrogen consumption for the B:C 0.5 oil compared to the other two oils is a result of both lower deoxygenation and hydrogenation. The hydrogen consumption during hydrotreating of the FP oil was around 0.1 g

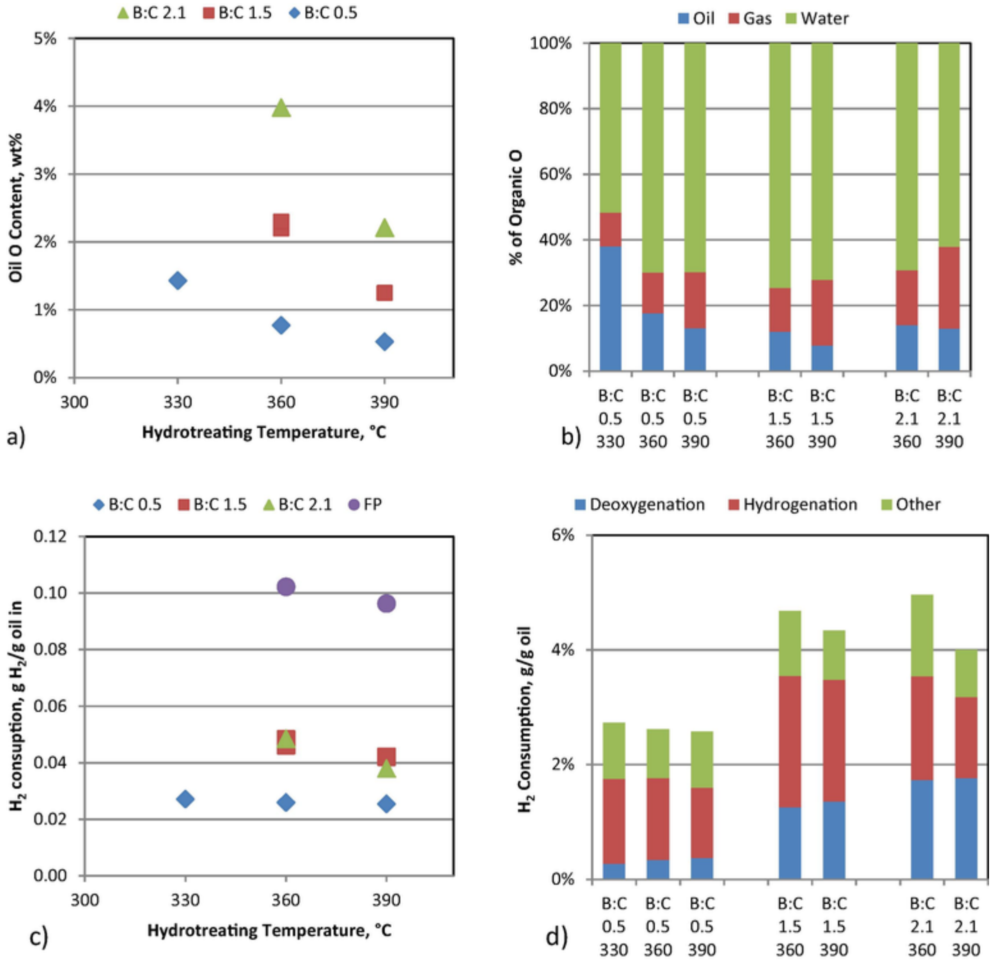

Fig. 3. a) Oxygen contents in the hydrotreated oils, b) fate of organic oxygen during hydrotreating, c) hydrogen consumption during hydrotreating, d) hydrogen consumption for oil deoxygenation and hydrogenation. For hydrogen consumption, other indicates the difference between total hydrogen consumption and hydrogen consumption calculated for deoxygenation and hydrogenation of oil.

H_2/g oil, i.e., twice as high as measured for the CFP oils. FP oils have large quantities of small oxygenated compounds such as hydroxyacetaldehyde, acetic acid, ethanedial, and methanol, which consume hydrogen but do not contribute to liquid products.

3.3. Integration of catalytic fast pyrolysis and hydrotreating

For cost-effective production of liquid transportation fuels via CFP and hydrotreating, integration and optimization of the two steps are required. The hydrotreating temperatures required to obtain oil with 1 wt% oxygen were estimated by interpolation or, as needed, by extrapolation from the plots of product oxygen contents vs. temperature in Fig. 3a, and the corresponding hydrogen consumption from the plots of hydrogen consumption vs. temperature in Fig. 3c. Fig. 6 illustrates the hydrotreating temperature and hydrogen consumption as well as carbon efficiencies for both the CFP and hydrotreating step. The data is shown as a function of the oxygen remaining in the CFP oil, which describes the CFP conditions more generally than the B:C ratio. The B:C ratio required to obtain a given oxygen content depends on the activity of the CFP catalyst.

The temperature required for hydrotreating increases as more oxygen is retained in the CFP oil. Beyond the increase in hydrotreating temperature, CFP oils with high oxygen content may require more than one hydrotreating stage, which would increase the hydrotreating costs. The hydrogen consumption shows a maximum due to the opposite trends for deoxygenation and hydrogenation. Hydrogen consumption for deoxygenation increases as the CFP oil oxygen content increases whereas hydrogen consumption for hydrogenation decreases as the CFP oil oxygen content increases due to reduced aromatics saturation at the higher hydrotreating temperatures required.

The carbon efficiency for CFP increases as more oxygen is retained in the CFP oils whereas the hydrotreating carbon efficiency decreases with more oxygen in the CFP oil. The carbon efficiency for hydrotreating of the CFP oils was remarkably high (over 90% in all cases). This agrees with the high yields reported in other studies [28,45]. The carbon yields in the current study were even higher than those reported earlier, likely due to lower oxygen contents of the CFP oils. Overall, the carbon efficiency is dominated by the efficiency of the CFP step. As discussed in Section 3.1, the condensation train for CFP was not optimal and some light condensable organic compounds were lost. Capturing these would have increased the CFP oil carbon yields by approximately 7%. Nevertheless, the carbon yields from CFP remain low compared to those from hydrotreating and the overall carbon yield is highly dependent on the CFP carbon yields. In order to improve the economics of biofuels production, it is thus vital to enhance the performance of the catalytic pyrolysis step. Research efforts should be concentrated on developing CFP catalysts that enhance carbon retention by reducing carbon loss to light gases and

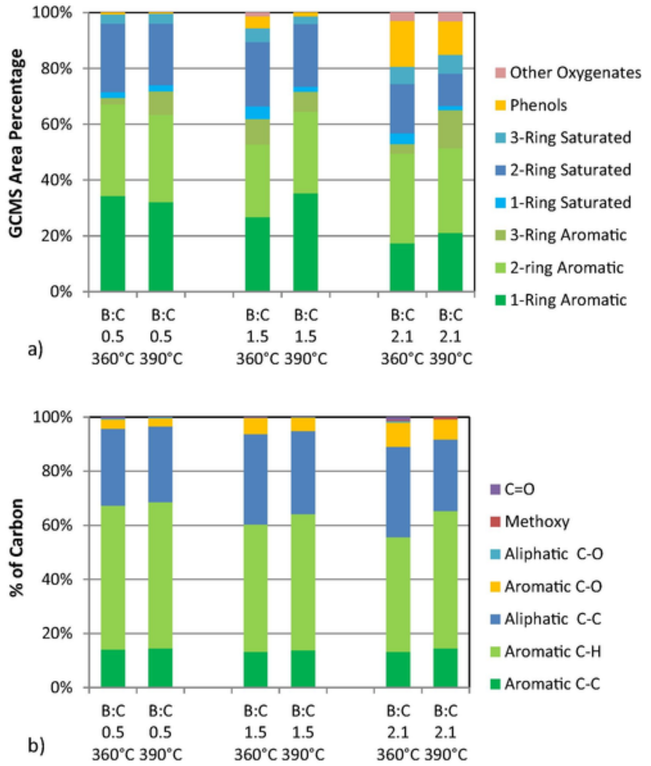

Fig. 4. a) GCMS analysis and b) ^{13}C NMR analysis of hydrotreated oils.

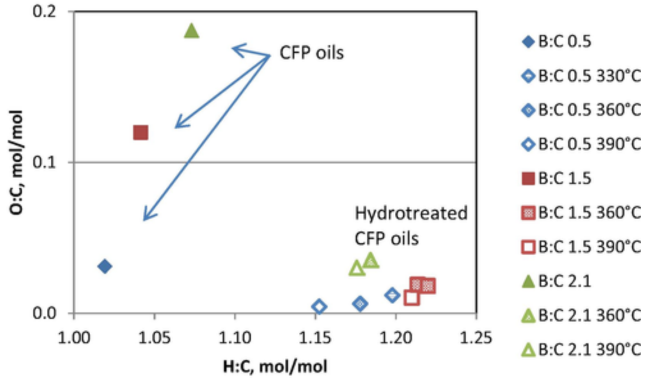

Fig. 5. van Krevelen diagram of the CFP oils before and after hydrotreating.

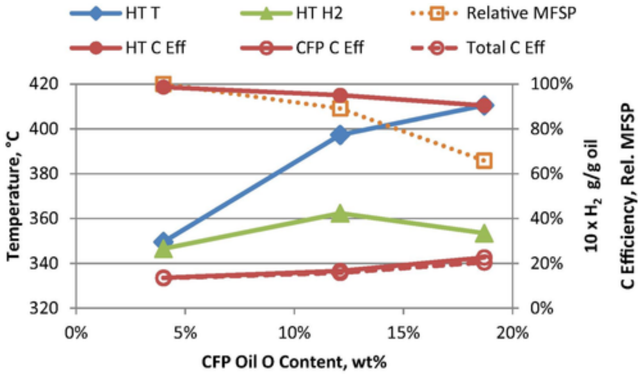

Fig. 6. The estimated trends for an overall process producing oil with 1 wt% of oxygen. Shown are hydrotreating temperature (HT T), hydrogen consumption during hydrotreating (HT H_2), carbon efficiency for the catalytic pyrolysis and hydrotreating steps and the overall process (CFP C Eff, HT C Eff, and Total C Eff, respectively), and relative Minimum Fuel Selling Price (MFSP).

coke while ensuring the production of CFP oil that can be efficiently deoxygenated by hydrotreating.

Few experimental results for CFP and hydrotreating are available in the literature, and these new experiments provide insight into process economics using HZSM-5 catalyst in an ex situ CFP configuration. Fig. 6 shows the relative Minimum Fuel Selling Prices (MFSP) versus the oxygen content retained in the CFP oil. For this analysis, we allocated the missing material proportionally among the different product phases. Further experiments may inform different distributions of the missing portions of the mass or carbon balances. However, since all cases were treated in the same manner, the impact on the relative MFSPs is likely not large. As highlighted by Dutta et al. [27], higher carbon efficiency towards liquid fuel blendstocks is one of the most important economic drivers.

Based on these results, with the current state of zeolite-based CFP catalysts, it is economically more attractive to preserve the carbon during CFP while leaving higher oxygen contents in the organic phase. There will, however, be an upper limit where acids and carbonyls are no longer insignificant in the CFP oil, and one-stage hydrotreating will not be feasible. CFP research continues to target improved carbon efficiencies by e.g. including catalytic activation and use of hydrogen during CFP to increase hydrodeoxygenation over decarboxylation and decarbonylation. With improved carbon efficiencies during CFP, the advantage of hydrotreating over CFP may no longer be valid.

Based on the results in this study, the improved CFP oil quality can reduce hydrotreating severity for achieving lower oxygen levels in the final product. These experiments also illustrate that hydrotreating and hydrodeoxygenation of CFP oils leveraging catalysts developed for the removal of other heteroatoms during petroleum refining is more mature and optimized than the current state of the art CFP using zeolite-based catalysts. Another important learning for technoeconomic modeling from these experiments is that the previously assumed hydroprocessing carbon efficiency for CFP oils (e.g. Figure 8 in [27]) may be conservative and the hydrotreating carbon efficiencies for CFP oils are likely higher. However, further experiments are necessary to corroborate these preliminary findings, as well as to understand the role of hydrocracking heavier fractions. In addition, the hydrotreating data used in Fig. 6 were extrapolated to a slight degree in some cases to project to oxygen contents below 1 wt%, and those extrapolations should also be validated experimentally.

4. Conclusion

Oils with a wide range of organic oxygen contents can be prepared by catalytic fast pyrolysis (CFP), and the CFP oils can be subsequently hydrotreated to produce oil with <1wt% oxygen. Higher severity during CFP results in lower oil oxygen content and fewer types of oxygenated species, with phenols being the most recalcitrant, but at low oil yield. With the current state of technology, leaving more oxygen in the CFP oil leads to better overall carbon efficiency and economics. Developing catalysts that provide higher carbon efficiency for the CFP step is vital for cost-effective production of hydrocarbon fuels.

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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.2017.06.098.

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