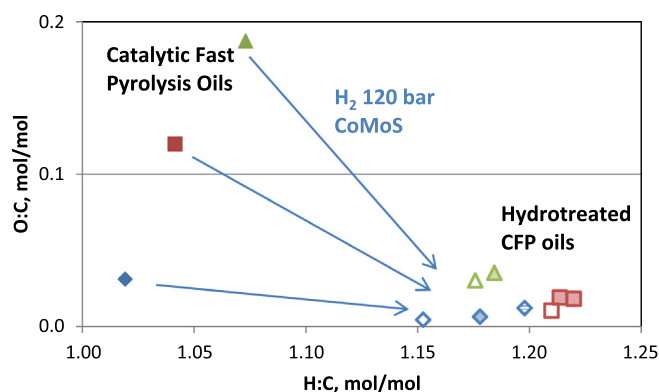Full Length Article

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

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GRAPHICAL ABSTRACT

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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.

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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

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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 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

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.