Catalytic pyrolysis for the production of refinery-ready biocrude oils from six different biomass sources

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Abstract

This study focused on understanding the impact of catalytic pyrolysis and biomass feedstock on the physicochemical properties of upgraded bio-oils. Results from catalytic conversion of different types of biomass feedstocks (***Woody***: pine, hybrid poplar and pinyon-juniper; ***herbaceous***: switchgrass; ***agricultural residue***: corn stover; and ***forest residue***: pine bark) with HZSM-5 zeolite to biocrude oils are presented. The study showed that the source of biomass plays an important role in catalytic pyrolysis products. Significant differences were observed in product distribution, selectivity to aromatic hydrocarbons and physicochemical properties of the biocrude oils. The pyroprobe-GC/MS experiment showed that pine and pinyon-juniper produced the highest carbon yield of monoaromatic hydrocarbons. ^{13}C NMR analysis revealed that aromatic hydrocarbon content of the oils followed this order: pinyon-juniper > corn stover > pine > poplar > switchgrass > pine bark. The chemical composition and the physicochemical properties indicated that it is critical to reduce carbonyls to achieve stable oils. Also, it was found that elimination of sugars (levoglucosan) and phenolics would improve oil specific gravity and viscosity. Furthermore, reducing the acidity of oils by catalytic pyrolysis appeared to be very challenging. Hence, phenols (weak acids) may have to be minimized in addition to other acids to increase the pH. The nitrogen contents correlated with pH values. Thus, feedstocks with high nitrogen content produced less acidic oils. Nonetheless, high content of nitrogenous compounds could make the biocrude oil highly unstable. The effects of the bio-oil chemical composition on the physicochemical properties are discussed as well as opportunities and challenges of utilizing biocrude oil as feed for standard refinery units.

1.0 Introduction

Co-processing of bio-oil with petroleum crude oil in standard refinery units is an attractive strategy in facilitating the production of hydrocarbon liquid fuels from renewable sources. The implementation of this refinery integration concept will greatly reduce the total capital investment required and the ramp-up time for producing transportation fuels in the gasoline, diesel and jet fuel ranges from biomass. Nonetheless, it is a challenge to co-process bio-oil alongside heavy petroleum feedstocks such as atmospheric gas oil (AGO) and vacuum gas oil (VGO) in traditional refineries. This is primarily due to the vast differences between the physicochemical properties of bio-oil and crude oil. The bio-oil is a mixture of oxygenates while the crude oil consists of mainly hydrocarbons. The plot of carbon yields versus molar O/C ratios of major compounds produced from the pyrolysis of hybrid poplar in Figure S1 underscores the fact that highly oxygenated species such as acetic acids (corrosive), hydroxyacetaldehyde (reactive), and levoglucosan (dense) are present in significant quantities in bio-oils. These chemical species are not attractive as fuel components because they negatively impact the physical property of the bio-oil. Hence, to leverage existing petroleum-refining infrastructure to produce transportation liquids from bio-oil, their fuel properties would have to meet acceptable standards in the refinery industry.

Catalytic pyrolysis of biomass is one of the promising technologies that improve the compatibility of bio-oils with petroleum refinery feedstocks. This technique has been extensively studied for over 20 years and it has been successfully shown to be able to convert biomass into less oxygenated fuel [1]. However, one of the areas often overlooked is the evaluation of how the catalytic process affects the physical properties of the upgraded bio-oil and its impact as a potential feedstock in a petroleum refinery. This is very important, because a refiner would like to know how the upgraded bio-oil compares to the assays of benchmark crude oils. It will also help with research strategies for insertion of upgraded bio-oils in a conventional refinery. For example, Table S1 shows the quality of upgraded bio-oils from catalytic pyrolysis of poplar.[2] It can be seen that the upgraded bio-oils (A and B) in comparison with the raw bio-oil were relatively stable, less viscous, less acidic, and were high in carbon content, API gravity,

3

and energy density. Considering these improved qualities, the upgraded bio-oils could be considered as a "biocrude" for co-feeding with AGO or VGO in an FCCU (fluid catalytic cracking unit).

Furthermore, it is important to understand how biomass feedstock influences the quality of the resulting bio-oil since larger scale production of upgraded bio-oils from catalytic pyrolysis operations will eventually rely on a diversity of feedstocks.[3] This is rarely investigated compared to studies that have been conducted on the effect of catalyst type and operating conditions. It should be pointed out that a wide variety of feedstocks have already been studied by different research groups. Nonetheless, attempts to ascertain the effect of each feedstock on the process and quality of the upgraded bio-oil from the large body of work in the literature is very challenging due to differences in catalysts, process conditions, reactor configurations and bio-oil phases. The commonly studied feedstocks include pine wood,[4-7] hybrid poplar, [8-12] corn cob,[13-15] and beech wood residue.[16, 17] Others include switchgrass, [15] oak wood, [18] maple wood,[19] aspen, [20] spruce wood,[21] rice husks, [22] miscanthus giganteus, [23] olive oil waste, [24, 25] oil seeds,[26] and bamboos[27] to name a few.

According to the U.S. Billion Ton update, [28] biomass for bioenergy would come from a variety of sources including agricultural crops, herbaceous energy crops, forests, various residue streams, and short rotation woody biomass. Hence, in this study, a number of significant U.S. biomass resources (***Woody***: pine, hybrid poplar and pinyon juniper (PJ); ***herbaceous***: switchgrass; ***agricultural residue***: corn stover; and ***forest residue***: pine bark) were investigated. The objective as discussed is to study the role of biomass feedstock on catalytic fast pyrolysis and the physicochemical fuel properties (elemental composition, long-term storage stability, acidity, viscosity, density, and solid residue) of the resulting bio-oil fraction (biocrude). The catalytic pyrolysis of the various feedstocks with ZSM-5 zeolite was studied on a pilot-scale fluidized bed reactor as well as in a pyroprobe reactor interfaced with GC/MS. The catalytic pyrolysis on the pilot scale described herein is slightly different from many reported studies. In this work, the non-condensable gases (NCG) were continuously recycled to provide a reducing reaction environment. This has been demonstrated to improve the overall process yields and energy balance.[10, 29]

4

2.0 Experimental Section

2.1 *Biomass Feedstocks*

All the biomass samples were dried, ground, and sized to 2 mm. Grinding was done in a Thomas Model 4 Wiley mill (Thomas Scientific). Hybrid poplar, pine and pine bark were obtained from Virginia Tech forestry club. Corn stover and switchgrass samples were supplied by Idaho National Laboratory. The pinyon juniper (PJ) wood chips were obtained through the Utah State office of U.S. Bureau of Land Management (BLM). The moisture content was determined using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). A Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK) was used to determine the C, H, N, O, and S contents of the various feedstocks (See Table S2).

2.2 *TGA-FTIR characterization of biomass feedstocks*

Prior to catalytic pyrolysis, the thermal decomposition of the biomass feedstocks were analyzed using TA Instruments Q500 (TA Instruments ,New Castle, DE) interfaced to a Nicolet Avatar, 370 DTGS series FTIR with a 1 in. stainless steel transfer line. Approximately 15 mg of each sample was subjected to thermogravimetric analysis at a heating rate of 20 ^{o}C/min from 25 to 750 ^{o}C with 60 mL/min of N_2 as carrier gas. The decomposition products from the TGA were purged through a flow cell with KBR crystal windows. Both the IR cell and the transfer line were maintained at a temperature of 225 ^{o}C. The spectra were obtained over a range of 4000-650cm^{-1} at a 4 cm^{-1} resolution and a background gain of 4.0 with 32 scans at about 35 s intervals providing time resolved FTIR spectra. The FTIR spectra were monitored at different temperature to characterize the gases that evolved during the analysis.

2.3 *Catalysts*

The acid catalyst used was a commercial HZSM-5 zeolite from Süd-Chemie Incorporated. The catalyst as received was crushed and sieved to homogenous particle size of 250-400 μm and calcined at 550 ^{o}C for 5 hours in a muffle furnace before testing. To evaluate the surface area of the catalyst, nitrogen adsorption

isotherms were determined using a Quantachrome Monosorb instrument (model MS-16, Quantachrome Instruments, Boynton Beach, FL, USA). The samples were degassed at 220 °C for 3 hours before the BET surface area measurements. The isotherms were used to calculate the Brunauer-Emmett-Teller (BET). The measured surface area was 325 m^2/g and the average bulk density was 0.50 g/cm^3.

2.4 *Pyroprobe catalytic pyrolysis (Py-GC/MS)*

Analytical catalytic pyrolysis of the various biomass feedstocks with ZSM-5 catalyst was conducted using a CDS Analytical Pyroprobe 5200 (CDS Analytical, PA) interfaced with Agilent 7890A gas chromatograph and 5975C mass spectrometer detector at Brookhaven National Laboratory (BNL). All the experiments were performed in a direct Py-GC/MS mode at atmospheric pressure. The catalyst-to- feed (CF) ratio was about 10 (w/w). Biomass samples of size of 0.3 to 0.6 mg were loaded into a quartz tube of 25 mm in length and 1.9 mm in diameter. The ZSM-5 catalysts were placed at both ends of the loaded sample in the quartz tube and they were held in place at the center with small plugs of quartz wool. The quartz tubes were weighed before and after pyrolysis using a Mettler Toledo MS105 semi-micro balance with sensitivity of 0.01 mg (Mettler Toledo, Greifensee, Switzerland). The Pyroprobe control software was programmed to rapidly heat the sample to 550 °C and hold for 20 s. However, the actual pyrolysis occurred at about 475 °C since the temperature inside the quartz tube was about 75 °C lower than the set point filament temperature. Each experiment was conducted at least five times to ensure reproducibility and accuracy of results. Detailed description of the GC/MS methodology can be found in previous study.[30] The GC column was calibrated with standard compounds for identification and quantification of peaks present in the catalytic pyrolysis products. The National Institute of Standards and Technology (NIST) mass spectral library and a custom library created for the mass spectra of the known compounds were both used in the identification of compounds. The analytical standards prepared for the calibration of the GC/MS system were purchased from Sigma-Aldrich. The calibration curves had R^2 value greater than 0.95.

2.5 *Pilot-scale catalytic pyrolysis with product gases recycling*

The catalytic pyrolysis of the biomass feedstocks were conducted in a 2 kg/h fluidized bed pyrolysis unit (Figure 1a) located at the Thermochemical Biomass Research Lab, Utah State University, UT. The reactor consists of a 4-in. schedule 10 pipe spool with a bed support and gas distributor at the bottom and a gas exhaust at the top. The reactor was externally heated to maintain an average operating temperature of 475 ^{o}C using a three-zone furnace (ATS Series 3210 Split Tube Furnace) rated for operation up to 1000°C. The biomass feedstock was fed continuously from a gravimetric, double-screw feeder (Brabender Technologie Inc.) through a ball valve into the hot fluidized bed containing about 1 kg ZSM-5 catalyst. The ball valve was employed to provide a pressure seal between the feeder and the fluidized bed. For each experiment, about 3 kg of biomass was fed to achieve a catalyst-to-feed ratio of 0.33 (w/w) by the end of the run. Initially, 1.0 standard cubic feet per minute (SCFM) of nitrogen was used for fluidization and after 10 min into the run, the nitrogen gas was gradually replaced with the NCG from the catalytic pyrolysis until the fluidizing gas was made up of 0.4 SCFM of nitrogen and 2.2 SCFM of syngas. During the process, the mixture of char, vapors and gases that exit from the reactor was separated by a high temperature filtration system maintained at 400 ^{o}C. The hot gas filter system consists of a 6-in schedule 10 pipe spool with a char collection cone and gas inlet port at the bottom. The separated gases and vapors were then passed through primary and secondary tube-in-shell heat exchangers as well as a venturi scrubber to condense the pyrolysis vapors and to quench the NCG. A process water chiller unit was used to provide a cooling medium for the three stage condensing system. The primary condenser utilized an indirect cooling loop to control condenser temperature, whereas, the secondary condenser used the direct cooling of the process chiller. The aerosol particles that escaped the venturi scrubber were captured by a wet electrostatic precipitator (WESP) maintained at 30 kV. The NCG were further cleaned with coalescing filters before entering a syngas compressor for recycling into the pyrolysis unit. The syngas compressor provided the gas pressure necessary for recirculation of syngas for fluidization. The entire process was remotely controlled and temperatures, pressures and gas flows were all monitored by

National Instrument's LabView and Fieldpoint embedded controller with input/output (I/O) modules. The evolved gases were analyzed online by a micro gas chromatography (Varian 490-GC). The micro GC is equipped with two modules, a 10 m Molsieve (MS) 5 Å column and a 10 m porous polymer (PPU) column. Each module is equipped with a thermal conductivity detector. The MS column was used to analyze H_2, CH_4 and CO. The PPU column was used to analyze CO_2 and C_1-C_4 gases. The yields of the products were determined gravimetrically, mass of char/coke was determined by weighing the hot gas filter collection canister and the reactor content before and after each pyrolysis experiment. The total mass of bio-oil was measured by weighing the condensers and electrostatic precipitator reservoirs before and after each experiment. The total mass of the non-condensable gas was determined by difference.

2.6 *Characterization of upgraded bio-oil (biocrude oil)*

The biocrude oils (organic fraction) collected after a complete run of 3 hours from the catalytic pyrolysis experiment were characterized for the following properties. The acidity was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 5-10 min stabilization of the mechanically stirred oil. The viscosity of the bio-oils was measured at 40 ^{o}C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were equivalent to viscosities determined by ASTM D445 method. The stability of the bio-oils was measured as a change in viscosity during storage at room temperatures. The bio-oils used for the studies were stored in a 100 mL air-tight glass vials sealed with a plastic cap under laboratory ambient conditions for a minimum of 12 months. Their viscosities were taken at the end of each six months period. The SVM 3000 Stabinger viscometer was also used to measure the densities of the oils. Calibrations were done prior to measurements with distilled water free from bubbles. Then, the API gravity of the oils was estimated from their specific gravities. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. 50 ml of methanol were placed in the titration vessel and conditioned. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent

and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass

was recorded. The chemical compositions of the bio-oils were analyzed by both Fourier-transform

infrared (FTIR) and carbon-13 nuclear magnetic resonance spectrometry (^{13}C NMR). For FTIR, about

150 mg of each sample was used to obtain a spectrum over a range of 4000-650 cm^{-1} using an IR

spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR. 32 scans at a 4 cm^{-1} resolution

and a background gain of 4.0 were used. The ^{13}C-NMR experiment was performed with 1.0 g of bio-oil

sample dissolved in 0.7 ml of deuterated dimethyl sulfoxide-d_6 in a 5 mm sample tube. The NMR solvent,

DMSO-d_6 [99.9 atom % D, containing 1% (v/v) tetramethylsilane (TMS)] was obtained from Sigma-

Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The ^{13}C-NMR spectra were recorded on a JOEL 300 MHz

NMR spectrometer (JEOL Ltd, Tokyo, Japan). The observing frequency for the ^{13}C nucleus was 100.58

MHz. The pulse width was 10 µs, the acquisition time was 1.58 s, and the relaxation delay was 2 s. The

spectra were obtained with 4000 scans and a sweep width of 20.0 KHz.

3.0 Results and Discussions

3.1 *Characterization of biomass feedstocks*

The elemental analysis in Table S2 shows that pine bark and the woody feedstocks (poplar, pine, and PJ)

had relatively higher carbon contents (50.3 - 53.4 wt.%) than that of switchgrass (48.1 wt.%) and corn

stover (46.5 wt.%). The hydrogen contents were comparable among the feedstocks with the exception of

poplar, which had the highest (6.0 wt.%). With regard to nitrogen content, switchgrass (0.65 wt.%) had

the highest, followed by corn stover (0.43 wt.%), PJ (0.34 wt.%) and then pine bark (0.22 wt.%). The ash

contents for corn stover (8.97 wt.%) and switchgrass (5.32 wt.%) were significantly higher than that of

the woody feedstocks. The high ash contents of the herbaceous feedstocks are due to the fact that they

contain higher amounts of inorganic matter. [3] The TGA studies indicated that the woody feedstocks had

high volatile matter (Figure S2). However, the non-volatiles (solid residue) were found to be high in pine

bark, switchgrass, and corn stover. The high formation of solid residue in pine bark is due to the high

content of tannins and lignin.[31] On the other hand, the high solid residue formed by switchgrass and corn stover was attributed to their high ash contents.[3]

The qualitative compositional analysis by TGA-FTIR indicated that the distribution of the biopolymers varied among the feedstocks. Based on the maximum rate of decomposition of xylan and microcrystalline cellulose, it can be inferred from the results that, switchgrass and corn stover had higher hemicellulose fractions while poplar and pine had higher cellulose contents (See Figures S3a and S3b). On the other hand, pine bark and PJ appeared to have higher lignin contents. Additional small decomposition peaks seen at 125, 485, and 650 ^{o}C in the pinyon-juniper DTG curve suggest that it had other minor components which were not obvious in the other feedstocks. The small peaks could be due to decomposition of constituents such as oleoresin (e.g., terpenes) [32] which are known to be reasonable high in PJ compared to other woody biomass.

The FTIR analysis of the degradation products: CO_2 (2321-2358 cm^{-1} and 671 cm^{-1}), CO (2115-2181 cm^{-1}), CH_4 (3016 cm^{-1}), and carbonyl compounds (1680-1800 cm^{-1}) as shown in Figures S4a, S4b, and S4c; complement the observations made on the structural differences between the feedstocks. In Figure S4b, it can be seen that CO_2 evolution due to the thermal breakdown of xylan was high in the spectra of switchgrass and corn stover. Also, it can be seen that the evolution of carbonyls and CO due to the breakdown of cellulose was intense in the spectra of poplar and pine (Figure S4c). These inferences from the qualitative structural analysis by the TGA-FTIR were in agreement with reported compositional analysis of similar feedstocks in the literature (See Table S3 for details).[31, 33, 34 35]

3.2 *Pyroprobe catalytic pyrolysis (Py-GCMS)*

Catalytic pyrolysis of the feedstocks with ZSM-5 in the pyroprobe at 550 ^{o}C and C/F ratio of 10 (w/w) produced primarily monoaromatics (benzene, toluene, xylene, ethylbenzene, and alkylbenzenes), naphthalenes, indene, indane, and PAHs. The monoaromatics were quantified and their carbon yields are shown in Table 1. The carbon yield is defined as the percentage of the carbon in the product with respect

to the carbon in the biomass on mass basis. The results showed that the highest carbon yield for benzene (1.6 %), toluene (2.2 %), ethylbenzene (1.5 %), and xylene (4.8 %) were produced from PJ. The highest carbon yield for alkylbenzenes (8.6%) was obtained from pine. Overall, the monoaromatics were higher for pine (17.7% carbon) and PJ (17.4% carbon). On the contrary, the lower carbon yields of monoaromatics were obtained from hybrid poplar (11.1%) and pine bark (12.6%). Polyaromatics which were not quantified were analyzed based on their relative peak areas in the total ion chromatogram (See Figure S5). Most of the yields of the polyaromatics were comparable among the feedstocks with the exception of naphthalenes which were found to be relatively high in the products from hybrid poplar and pine wood. With regards to indenes, pine bark was found to produce the lowest. It is worth noting that some oxygenates (acetic acid and phenols) were present in the product distribution. This is probably due to catalyst deactivation. In comparison, switchgrass and corn stover produced slightly higher amounts of these oxygenated species.

The results indicate that the production of hydrocarbons from biomass using ZSM-5 is dependent on the type of feedstock. In a recent study on catalytic pyrolysis of the main structural components of biomass; it was reported that the yield of aromatic hydrocarbons decreased in this order: cellulose > hemicellulose > lignin.[36] This suggests that the amount of each biopolymer in the biomass affects the yield of hydrocarbons. Additionally, it can be inferred from this work that the chemical composition of the biopolymer can also affect the hydrocarbon yield. Particularly, differences in the type of lignin monolignols or hemicellulose units and other minor component could affect the selectivity of the biomass to hydrocarbons. Thus, feedstocks with similar amount of biopolymers could produce dissimilar yields due to fundamental differences in the structure of lignin or hemicellulose. As an illustration, hybrid poplar and pine generally have comparable amounts of biopolymers (see Table S3); but the overall monoaromatic yield from pine was about 50% more than that produced from hybrid poplar. This could be because, the lignin in pine (softwood) produces more guaiacols (one methoxy group) intermediates and the lignin in poplar (hardwood) forms more syringols (two methoxy groups) intermediates. In such a case,

differences in the reactivity of syringols and guaiacols with ZSM-5 could affect the yield of aromatic hydrocarbons. Gyubo et al. [37-39] have shown that pyrolysis intermediates such as phenols, aldehydes, ketones, and acids react differently with ZSM-5 catalyst. Generally, methoxylated phenols were found to have low reactivity to hydrocarbons on ZSM-5.[37] Hence, the high degree of methoxylation in the phenolic intermediates from poplar may explain why the aromatic yield was lower than that of pine. The results from pine bark also suggest that feedstocks rich in polyphenols may have low selectivity to hydrocarbons. It should be mentioned that other components in the feedstock such as alkali matter and nitrogen contents could reduce conversion to hydrocarbons as a result of catalyst contamination. This may explain the moderate yields of aromatics produced by switchgrass and corn stover. On the other hand, other residual constituents such as resins in pinyon-juniper seem not to have a negative impact on its conversion to hydrocarbons. In general, the results suggest that pines and junipers could be considered as better feedstocks for the production of biocrude oils.

3.3 *Pilot-scale catalytic pyrolysis product distribution*

Figure 1b shows a typical process temperature profile for the pilot-scale catalytic pyrolysis process. The temperatures across the ZSM-5 catalyst bed in the fluidized-bed reactor were between 475 and 500 $^{\circ}$C. It can be seen that the fluid-bed temperature profiles (Fluid Temp. 1, 2, and 3) of the three thermocouples at the bottom, middle, and top of the catalysts bed were similar. This is an indication that the bed was well-mixed due to good fluidization. The condensation system temperatures show that the hot vapors and gases that exited the gas filter at around 325 $^{\circ}$C were cooled to about 170 $^{\circ}$C in the primary condenser and to about 25 $^{\circ}$C in the secondary condenser.

Table 2 summarizes the catalytic pyrolysis products distribution for the various feedstocks. The total liquid yield represents the liquid products collected from the two condensers and the WESP. The char/coke refers to the summative yield of the char produced and the coke formed on the HZSM-5 catalyst. From the results, it can be seen that an average liquid yield of about 40 wt.% was produced from

most of the feedstocks with the exception of corn stover (31 wt.%) and pine bark (35 wt.%) which gave

relatively lower liquid yields. The yield of the oils collected from the WESP varied between 5.3 and 10.2

wt% while the condenser fractions were between 29.2 and 37.6 wt.%. Overall, pine wood produced the

highest liquid yield (42.5 wt.%). The pilot-scale liquid yields in this study were comparable to those

reported by Iliopoulo et al..[40]

The char/coke yield decreased as follows: pine bark > corn stover > switchgrass > PJ > pine >

polar. The yield from pine bark was 33.4 wt.% and that from hybrid poplar was 17.0 wt.%. The trend in

the char/coke yield was found to correlate with the ash contents of the feedstocks. The char/yield from

pine bark was an exception. As expected, feedstocks with high ash contents would relatively form more

char. Hence, it can be seen that corn stover and switchgrass which contain higher levels of ash had

relatively higher char/coke yields. In comparison, hybrid poplar and pine with lower ash contents had

lower char/coke yields. It is also important to realize that PJ which had ash content comparable to both

poplar and pine; however, it produced relatively higher char/coke yields (22.8 wt.%). This may be due to

the presence of the minor high molecular weight (HMW) components as seen in the DTG analysis. On the

other hand, the high amount of char/coke formed by pine bark was attributed to the high content of lignin

and tannins. [31]

The non-condensable gas (NCG) yields were found to be relatively higher for the woody biomass

compared to switchgrass, corn stover, and pine bark. To evaluate the effect of the feedstocks on the NCG,

the concentration of H_2, CH_4, CO CO_2 and C_1-C_5 gases were monitored at a time interval of 3.5 mins

during the 3 h run. The average compositions (mol %) of the NCG produced by each biomass is shown

also in Table 2. The results indicated that the carbon oxides were the predominant gases formed and they

constituted about 80% of the product gas. The light hydrocarbon gases including CH_4 varied between 12-

18 % while H_2 gas was between 3-5 %. The woody feedstocks were found to produce more CO. In

contrast, higher fraction of CO_2 was produced from switchgrass, corn stover and pine bark. The molar

ratio of CO/CO_2 ranged from 1.2-2.0 and increased in this order: pine > hybrid poplar > pinyon juniper >

pine bark > corn stover > switchgrass. The fraction of light hydrocarbons including CH_4 in the product gas was highest for pinyon-juniper and lowest for pine bark. In catalytic pyrolysis, deoxygenation of the primary pyrolysis vapors occurs through the formation of CO_2, CO and H_2O. Therefore, the results indicate that feedstock with high hemicellulose content rejects oxygen mainly as CO_2 through decarboxylation; and biomass with high cellulose content rejects oxygen predominantly as CO through decarbonylation. This observation is consistent with previous studies that show that the catalytic rejection of oxygen by ZSM-5 zeolite for carboxyl groups is through CO_2 and H_2O, while for carbonyl groups, it is largely through CO.[37-39, 41, 42] The gas composition analysis indicate that the characteristic of the biomass affect the reaction pathways during catalytic pyrolysis.

3.4 *Catalyst deactivation monitored by GC analysis*

The composition of the product gases changed marginally over the course of the experiment due to possible deactivation of the ZSM-5 catalyst. During catalytic pyrolysis, carbonaceous residues (coke) deposition on the zeolites can cause pore blockage and poising of the acid sites. As can be seen in Figure S6, the concentration of C_2-C_5 light hydrocarbons (mostly propylene and butene) was affected the most and a gradual decrease from the start to the end of the experiment was observed for all the feedstocks. The concentration of CO_2 also appeared to have decreased over time with the exception of the switchgrass run. A decrease in CO concentration was more evident with corn stover and pine. In contrast, the concentrations of CH_4 and H_2 increased progressively throughout the experiment.

To evaluate deactivation of the catalyst, the C_2-C_5 light hydrocarbons composition was used as a metric since ZSM-5 is known to be shape selective for the production of olefins as well as aromatics. Thus, a decrease in C_2-C_5 hydrocarbons over time signifies a decrease in the selectivity of the catalyst. Based on that, it appeared the ZSM-5 suffered considerable deactivation in the runs with switchgrass and corn stover. A significant decrease in the concentration of C_2-C_5 hydrocarbons at the end of the experiment was seen in the run with switchgrass (about 65%) and corn stover (47%). The percentage

14

decrease in the concentration of C_2-C_5 hydrocarbons for pine, poplar, pine bark, pinyon-juniper were all

relatively lower (about 28%). From the results, it is possible that the high content of nitrogen and

alkali/alkaline earth metals in switchgrass and corn stover may have caused deactivation of the zeolites

due to poisoning of the acid sites. In a recent catalytic pyrolysis study by Mullen and Boateng,[43] it was

found that inorganics in switchgrass can accumulate on the ZSM-5 zeolite and a consequently affect the

selectivity of the catalyst. Therefore, biomass feedstocks with high nitrogen and ash contents have high

probability for catalyst poisoning.

3.5 *Physicochemical properties of the biocrude oils*

Table 3 is a summary of the elemental composition and the physical properties of the biocrude oils. All

the biocrude oils (BCOs) were free-flowing homogenous organic liquids with a tint of dark-brown color.

The BCO from switchgrass was slightly different; it was more brownish, had a different strong odor and a

layer of thin film on the surface upon collection. In general, the biocrude oils had high carbon contents

and low oxygen contents. The carbon content varied between 73 -81 % and the oxygen levels ranged from

12-21%. The hydrogen and nitrogen contents were below 7.0 % and 2.2% respectively. From the results,

the BCO derived from pinyon juniper had the highest carbon content (80.24 %) and consequently the

lowest oxygen content (12.29 %). In contrast, the oil produced from hybrid poplar had the lowest carbon

content (73.3%) and highest oxygen content (20.3%). Notably, the oil from switchgrass had the highest

nitrogen (2.1 %) and hydrogen (7.0%) contents. In comparison, the oils from pine and hybrid poplar had

the lowest nitrogen contents (< 0.25%). All the sulfur levels in the oils were below detection limits. The

elemental compositions clearly show that the oils produced were relatively less oxygenated compared to

typical bio-oils produced by conventional pyrolysis. [2, 44-46]

In terms of acidity, the oils from hybrid poplar, pine and pine bark had pH values of 3.66, 3.71

and 4.03 respectively. Among the woody feedstocks, the PJ biocrude had a relatively higher pH value

(4.51). Overall, the switchgrass oil had the highest pH value (5.00) followed by corn stover oil with a pH

value of 4.58. This suggests that herbaceous energy crops and agricultural residues produce relatively less

corrosive oils compared to woody biomass. The viscosity of pine bark (90.9 cSt) and switchgrass (87.5

cSt) BCOs were the highest. The oils with the lowest viscosities were produced from PJ (15.3 cSt) and

corn stover (23.7 cSt). It should be pointed out that all the organic fractions had comparable moisture

contents (3.1-4.9 wt.%), hence, the significant differences in the viscosities reported is not due to the

presence of water. The densities reported for the oils were high and ranged between (1.06 -1.14 g/cm3).

Consequently, the estimated API gravities were negative for most of the oils with exception of the PJ (2

^{o}API).

Figure S7 shows linear viscosity curves for the BCOs during a long term storage period of 12

months. From the results, it can be seen that the PJ oil was the most stable and the switchgrass oil was the

least stable. Clearly, the PJ oil barely changed and its rate of viscosity change over the 12 months of

storage period was 0.07 cSt/day. The BCOs from con stover, pine bark and the woody biomass feedstocks

could be considered relatively stable when compared with the switchgrass oil. It is worth noting that even

though pine bark and switchgrass had similar viscosities when produced; the rate of change in viscosity

for switchgrass was considerably higher than pine bark. The average rate of viscosity change for

switchgrass was 1.18 cSt/day and that of pine bark was 0.41 cSt.

The thermal degradation behaviors studied by TGA (Figure S8) also revealed major differences

in the biocrude oils. The amount of residue formed at 550 ^{o}C was used as a metric to measure the relative

coke-forming propensity of the BCOs. The results as shown in the properties table indicate that the oil

from PJ contained higher (~90 wt.%) fraction of components that degrade/volatilize below 400 ^{o}C.

Consequently, the PJ oil formed relatively lower amount (8 wt.%) of solid residue. The corn stover

biocrude was also found to behave similarly to the PJ oil. About 87.5 wt% of it degraded up to 400 ^{o}C and

10 wt% formed solid residue. Conversely, the oils from other feedstocks, particularly, hybrid poplar and

switchgrass showed a higher propensity to form higher amounts of solids when subjected to thermal

processing. The switchgrass and poplar oils formed respectively 14.6 and 15.6 wt% of carbon residue

and their fractions that degraded/volatilized below 400 ^{o}C were about 81.5 wt.%. The physicochemical

properties confirm that biocrude oils from different feedstocks have different characteristics and that the

starting biomass plays a major role in the quality of the resulting oil irrespective of the catalytic upgrading

step. The results also imply that different optimized operating parameters would be required for different

feedstocks in order to produce biocrude oils of equal quality.

3.6 *Characterization of the biocrude oils by ^{13}C NMR and FTIR*

^{13}C NMR and FTIR spectrometry were used to identify the various chemical functionalities in the

biocrude oils (BCOs). The compositional analysis using ^{13}C NMR was done by integrating the chemical

shifts of the following functional groups between 210 and 0 ppm as shown in Figure S9; aliphatic side

chains (δ 40-0 ppm), methoxy carbon in guaiacyl and syringyl moties (δ 57-55 ppm), alcohols, ethers and

anhydrosugars (δ 103-60 ppm), aromatics including phenols (δ 160-105 ppm), carboxylic acids and its

derivatives (δ 180-160 ppm), and ketones/aldehydes (δ 210-180 ppm).

The distribution of the types of carbon is provided in Table S4. It can be seen that the aromatic C-

C bonds (140-125 ppm) indicative of hydrocarbons such as benzene, alkylbenzenes and naphthalenes

were dominant in PJ, corn stover and pine BCOs. On the other hand, aliphatic C-C bonds were highest in

the switchgrass oil. The total C-C bonds (aliphatic and aromatic) in the BCOs decreased as follows: PJ >

corn stover > pine > poplar > switchgrass > pine bark. The methoxy carbon indicative of methoxylated

phenolics was highest in the oil from hybrid poplar. The overall phenolic carbon content based on the

aromatic C-OH bond signals (160 and 140 ppm), aromatic C-H bonds (125-105 ppm), and the methoxy

carbons; was highest for the BCO from pine bark. The total aliphatic C-O carbon content including the

levoglucosan carbons at 65.3, 72, 73.9, 74.1, 76.9 and 102.6 ppm decreased in this order: pine bark >

poplar > pine > switchgrass > corn stover > PJ. Finally, the carbonyl carbons decreased as follows:

switchgrass > corn stover > poplar> pine bark> pine > PJ. The^{13}C NMR results indicate that the biocrude

oils from PJ, pine, and corn stover were rich in aromatic hydrocarbons. In contrast, the biocrude oils from

poplar, switchgrass, and pine bark had relatively higher fractions of oxygenated compounds. Also, the

high content of methoxy carbons in the poplar BCO indicates that the methoxylated phenolic

intermediates were less reactive with ZSM-5. This could explain why the biocrude oil from poplar had

lower aromatic C-C bond signals and also why it poplar produced lower hydrocarbon yields in the Py-

GCMS experiment. The relatively high content of carbonyl carbons in switchgrass and corn stover BCOs

is partly due to signals from ketones and nitrogenous compounds (e.g. amides). As shown in Figure S10,

the carbonyl absorption band between 1650 and 1715 cm^{-1} was distinctively intense in the biocrude oils

from switchgrass and corn stover. The intense absorption band around 1700 cm^{-1} is indicative of ketones

and the notable shoulder around 1675 cm^{-1} is likely due to the presence of amide carbonyl. The N-H

stretch absorption at 3200 cm^{-1} seen especially in the switchgrass biocrude confirmed the presence of N-

containing compounds. The weak-to-moderate C-H stretching bands between 3100-3000 cm^{-1} and the C-

H bending between 900-670 cm^{-1} confirmed that aromatic hydrocarbon were more pronounce in BCOs

from PJ, pine, corn stover than switchgrass and poplar. The O-H stretching vibration around 3350 cm^{-1}

due to phenolic compounds was high in intensity for biocrude oils produced from poplar, pine and

switchgrass. In summary, the ^{13}C NMR and FTIR spectrometric analyses show that the chemical

composition of the biocrude oils differed as a result of the biomass source. Based on the various groups of

compounds identified, it can be inferred from the results that deoxygenation of the primary pyrolysis

vapor into hydrocarbons by ZSM-5 zeolite on the pilot-scale was very effective with pinyon-juniper, pine

and corn stover feedstocks.

3.7 *Effect of chemical composition on the properties of the biocrude oils*

To evaluate the effect of the oil composition on its physicochemical properties; a correlation between the

different types of carbons determined by ^{13}C NMR and selected properties were established. Significant

relationship between the elemental composition of the oils and the properties were also determined. The

Pearson correlation coefficients which are similar to classical linear correlation coefficients were

computed using XLSTAT package and the output is provided in Table S5. The results indicated a

significant negative correlation between the viscosity of the biocrude oils and the aromatic C-C bonds. In

Figure 2a, it can be seen that as the aromatic C-C bonds increased, the viscosity of the BCOs decreased.

This shows that the formation of hydrocarbons decreases the viscosity of the biocrude oil. It also explains

why the BCOs from PJ and corn stover had lower viscosities. On the contrary, a positive correlation was

found between viscosity and the content of oxygenated carbons, particularly the phenolic carbons (See

Figure S11a). Thus, it can be inferred that the presence of multifunctional phenolics in the oil contributes

significantly to the high viscosities seen in pyrolysis oils. This makes sense since viscosity is

fundamentally related to molecular weight. With regards to density, the results showed that high content

of levoglucosan increases the density of the oils and consequently lower the API gravity (Figure 2b). This

means, levoglucosan and probably the phenolic contents in the oils would have to be reduced below what

has been reported in this study to have a desirable impact on the density and the API gravity.

Additionally, it can be seen in Figure 2c that increase in the total C-C bonds decreases the density of the

oils. Hence, it is important for the biocrude oil to have high hydrocarbon content in order for it to have

high API gravity. For acidity, the pH values were found to correlate with the nitrogen content of the oils

(Figure 2d). This suggests that, nitrogenous compounds present in the oils had a basicity effect on the

oils. Thus, the higher pH values obtained from switchgrass and corn stover BCOs is probably because of

the presence of N-containing compounds.

Furthermore, the storage instability in terms of the rate of change in viscosity was found to have a

positive correlation with the content of carbonyl carbons. In Figure 2e, it can be seen that the instability of

the oil increases as the carbonyl content increases. This finding is consistent with the work by Oasmaa [47]

where carbonyl functionalities were reported to be responsible for the unstable nature of pyrolysis oils.

The correlation may explain why high instability behavior was observed with the oil produced from

switchgrass since it had the highest carbonyl content. Nonetheless, it should be mentioned that the

presence of heteroatomic compounds such as N-containing compounds in the switchgrass oil could be

part of the reason why it aged significantly. Studies have shown that the presence of both nitrogenous

compounds (amides) and reactive oxygenated functionalities do have adverse synergistic effect on the

stability of the bio-oils. [48] The storage instability of the oils was also found to have a negative correlation

with the aromatic C-C bonds (Figure S11b). This could indicate that the aromatic hydrocarbons inhibits

aging of oils or slows down the change in viscosity by having a solubilizing effect on high molecular

weight compounds in the biocrude oil. Finally, it was found that oils with high carbon content tend to

form less amount of solid residue when it undergoes thermal processing. Figure 2f shows the relationship

between the amounts of solid residue formed by the oils and the carbon content of the oils. The results

imply that biocrude oils with higher carbon content could be distilled without high formation of solids.

Also, Figure S11c suggests that levoglucosan and phenolics may have to be removed to reduce the

tendency of the biocrude oil to form solid residue/coke during further processing. In general, the

improvement in the properties of the oils produced from catalytic pyrolysis is dependent on the classes of

hydrocarbons produced and the type of oxygenated functionalities remaining in the upgraded bio-oil. It is

worth mentioning that the bulk oxygen content of the BCOs was found not to provide enough information

about the physiochemical properties of the oil. Importantly, there was no statistically significant

relationship between oxygen content and stability for example. Hence, its usage as a metric in

determining the stability and quality of pyrolysis as is the case in literature appears to be limiting.

3.8 *Opportunities and challenges of biocrude oil as a feed for standard refinery units*

As demonstrated in this study and other previous work,[2, 8, 44] the production of partially upgraded bio-oils

with improved fuel properties is achievable with zeolite based-catalysts. Eventually, the optimization of

the process parameters and configuration for different feedstocks would lead to the production of

biocrude oils with better fuel quality. Such improved bio-oils produced by catalytic pyrolysis could

potentially be processed alongside petroleum crude oil in standard refinery units. Among several options

available for integrating biocrude oil in traditional refineries, the fluid catalytic cracking unit (FCCU)

operation appears to be receiving a lot of attention as a viable option. This may be because of the known

flexibility in FCC process to respond to changing feedstock (Resid cracking), product requirement (High

octane number) and environmental regulations (NO_x and SO_x control).

In recent years, co-processing petroleum feedstocks with partially upgraded bio-oils to produce hydrocarbon fuels have been demonstrated by a number of research groups. Agblevor et al. [49] showed that about 15 wt% of stable biocrude oil with oxygen content levels of 20-25% can be co-cracked with 85 wt% standard gas oil in an FCC unit without negatively impacting the conversion to cracked products.[49] Likewise, Mercader et al.[50] showed that bio-oils with oxygen content as high as 28 wt.% could be co-processed successfully with FCC feed. So far, these studies suggest that the biocrude oil need not to be completely deoxygenated before it can be used as a refinery feed. Notwithstanding, a study by Fogassy et al.[51] points out that FCC co-processing of bio-oil (21% of oxygen) with VGO in a ratio of 10/90 (wt/wt) increases the formation of undesirable cracked products such as coke and light gases. This suggests that oxygen content beyond a certain limit in the bio-oil could be problematic. Thegarid and co-workers[52] in a study on co-processing catalytic pyrolysis oil (CPO) with VGO in FCC unit suggests that CPO can be directly cracked with VGO up to 20wt% without affecting the yields.

With these studies in mind, it is important to look at major factors that would make bio-oils an attractive feed. In general, a refiner would like to know the fuel properties of the biocrude prior to its insertion in a refinery to ensure that product yields and operationability are not negatively impacted. Therefore, to avoid potential adverse effect of co-processing, properties such as acidity, API gravity, viscosity, storage stability, distillation curves, elemental composition, miscibility and carbon residue of a biomass derived feedstock would have to be improved prior to its insertion in a refinery. A recent review paper by Talmadge and co-workers[53] points out the importance of understanding how an upgrading step such as catalytic pyrolysis for instance, influence the physicochemical property of the resulting upgraded oil and subsequently, its insertion into a petroleum refinery.

3.8.1 *Acidity*

The acidity of bio-oils is one of the major issues of concern. Keiser et al.[54] have shown that the acidity of bio-oil contributes corrosion and stress cracking in mild and low alloy steels. In this work, the BCOs produced had pH values between 3.7 and 5.0. Although these pH values indicate improvement in the

21

acidity of the oils, they are still high for a refinery feed. In the petroleum industries, the corrosiveness and acidity of the crude oils is characterized by TAN. Based on measurements of TAN on biocrude oils in a previous study,[8] it suggests that, bio-oil with a pH value higher than 3.7 would approximately have a TAN of about 41 mg/g and below. Typically, crude oils with TAN higher than 0.5 are considered acidic.[55] Considering this fact, it appears very challenging to achieve very low TAN levels by catalytic pyrolysis exclusively. Also, it is worth pointing out that the removal of carboxylic acids from bio-oils does not warrant higher pH values. In a previous investigation,[2] it was found that biocrude oil produced from hybrid poplar which barely showed carboxyl carbons (^{13}CNMR) had a pH of 4.05. Thus, other acidic contributing compounds such as phenolics (weak acids) would have to be decreased considerably as well to attain lower TAN numbers. In spite of this hurdle, it is expected that co-processing at lower percentages (e.g. 5-15 wt%) of biocrude oils with pH values as reported herein to have a minor impact due to dilution effect by the crude oil.

3.8.2 *Density/API gravity*

The density/API gravity is an important physical property and one of the simplest metric used to measure crude oil quality relative to Brent and West Texas Intermediate (reference oils). Normally, petroleum crude oils have API gravities between 19 and 50.[53] High-gravity crude oils are considered thin and are desirable because they have high value. In contrast, low-gravity oils are deemed heavy and they have less value because it costs more to refine heavy oils. The BCOs produced were of relatively high densities which caused them to have negative estimated gravities. Crude oils with API values below 10° are characterized as "extra heavy oil". This means that, the biocrude oils would be considered as extra heavy oils. To make the BCOs more attractive, the densities/API gravities would have to be improved and this requires substantial reduction in levoglucosan and phenolics contents in the oils. Nonetheless, this can be done to a limit as studies suggest, because, complete conversion of all pyrolysis oxygenates over ZSM-5 would mainly produce aromatic hydrocarbons which are also relatively denser than aliphatic hydrocarbons.[53] For instance, an oil with negligible concentration of levoglucosan and high amount of

aromatic hydrocarbons was found to have a density of 0.96 g/cm^3 and a corresponding API of 15.9°.[2] It can be seen that these values still fall within the range of heavy oils in spite of the high concentration of aromatic hydrocarbons.

3.8.3 *Stability and carbon residue*

Equally important properties to consider include stability and carbon residue. Both thermal and storage instabilities can inform a refiner about the behavior of the oil when subjected to refining unit operations. Studies have shown that stable biocrude oils can be distilled without high formation of solid residue.[2, 8] Contrary to that, unstable bio-oils are very difficult to distill. They usually polymerize during distillation as a result of the presence of reactive oxygenates and non-volatiles which could result in the formation of solid residue up to 50 wt. %. Another point to bear in mind is that, at the refinery, FCC feed such as VGO, could be charged from storage and is also preheated to about 229 $^\circ$C before entering the processing unit.[56] Thus, it is important for BCOs to be stable in order to prevent the occurrence of polymerization reactions during storage and at elevated temperatures. The carbon residue of the oils is also a critical property in FCC operations. It provides information about the coke tendency of the oil. In this work, TGA residue at 550 $^\circ$C was used as metric to measure the relative coke-forming propensity of the BCOs. The yield of the residues was dependent on the biomass feedstock and ranged from 8-16%. This means that the oils that form high amount of residue will most likely have a higher propensity to produce higher amount of carbon deposits during refining operations and consequently lead to high coke yields and catalyst deactivation. Hence, the stability and solid residue of the bio-oil could be used as a criterion to determine its processability in conventional refineries.

3.8.4 *Viscosity*

Viscosity is another property that is of interest, especially when it comes to transportation of the feed. Preferably, crude oil is transported to the refinery through pipelines because of the economic benefits associated with that approach.[57] This means that the viscosity of the biocrude oil must be within certain limits to ensure flowability. In fact, most crude oils transported by pipelines must have a maximum

viscosity of 400 cP. [57, 58] Thus bio-oils with viscosities higher than 400 cP at 25 ^{o}C would have to be reduced to avoid clogging of pipes, high-pressure drops and breaks in production. The initial viscosities of all the BCOs produced in this study were below 100 cSt at 40 ^{o}C. The lowest viscosity was 15.3 cSt and the highest was 91 cSt. These viscosities are actually desirable considering the fact that they had very low water content (5wt% max). Additionally, the BCOs were less viscous in comparison to heavy crude oils (10^{3} to 10^{6} cP at 25 ^{o}C).[59] Nonetheless, aging of the BCOs would result in significant increase in viscosity which could be problematic. As noted, some of the oils at room temperature storage aged at a rate of viscosity change of 1.18 cSt/day. Another point to bear in mind is, dedicated heated pipelines may be required to reduce and ensure that the viscosities of the biocrude oils are within specification. However, this approach results in added capital and operational cost. Therefore, it is best to have a less viscous and stable biocrude oil that could use existing pipelines without any hurdles.

3.8.5 *Elemental composition*

Finally, knowledge of the elemental composition of the biocrude oil is essential as it will inform which strategy to use in refining the biocrude. The results showed that the BCOs had high carbon content (73-81 %) but also had high oxygen (12-21%) and nitrogen (0.19-2.2%) levels. They were clearly deficient of hydrogen and the contents were below 7.2%. In comparison, heavy crude oil consists mainly of carbon (83-87%) and hydrogen (10-14%) with other minor contents such as sulfur, nitrogen, oxygen and metals.[57] For the biocrude oils, the lack of high sulfur content makes it attractive. Nevertheless, all heteroatoms and metals in crude oil are considered contaminants as they cause catalyst poisoning. Also, co-feeding high oxygen-content biocrude oil could affect the carbon efficiency of the process. Thus, it implies that BCOs with high nitrogen and oxygen contents would probably have to be pretreated further prior to its use as an FCC feed to avoid negative effects.

4.0 Conclusions

Catalytic pyrolysis with product gas recycle was conducted on different biomass feedstocks using HZSM-5 catalyst in a 2 kg/h fluidized bed reactor. Pyroprobe-GC/MS and TGA-FTIR studies were performed as

well. This work has demonstrated that biomass characteristics (structural components and extraneous materials) have significant influence on the yield and physicochemical properties of the upgraded bio-oils. The findings indicate that woody feedstocks give higher liquid yield while the herbaceous crop, agricultural, and forest residue form relatively higher amount of char/coke. Results from Py-GC/MS and ^{13}C NMR suggest that conifers (pines and junipers) are better lignocellulosic feedstocks for the production of hydrocarbon rich biocrude oils. It was also shown that oxygen rejection by decarbonylation to CO was dominant with feedstocks with high cellulose content but decarboxylation to CO_2 was higher in feedstocks with higher hemicellulose content.

Overall, the oil produced from pinyon-juniper had the highest carbon content (80.2%); was the most stable (0.07 cSt/day), less viscous (15.3 cSt), less dense (1.06 g/cm3) and the least oxygenated (oxygen of 12.3%). On the contrary, the bio-oil from switchgrass was the most unstable (1.18 cst/day) but the least acidic; the oil from pine bark was the most viscous (91 cSt) and heaviest (1.14 g/cm3); the oil from poplar was the most oxygenated (oxygen of 20.3%) and formed the highest amount of residue (15.6%) at 550 $^{\circ}$C when thermally degraded. In conclusion, the findings suggest that residual oxygenated species and nitrogenous compounds continue to negatively impact the fuel properties of an upgraded bio-oil.

Acknowledgement

REFERENCES

1. A. V. Bridgwater, *Biomass and Bioenergy*, 2012, **38**, 68-94.
2. O. Mante and F. Agblevor, *Biomass Conversion and Biorefinery*, 2011, **1**, 203-215.
3. D. Carpenter, T. L. Westover, S. Czernik and W. Jablonski, *Green Chemistry*, 2014.
4. S. Thangalazhy-Gopakumar, S. Adhikari, R. B. Gupta, M. Tu and S. Taylor, *Bioresour. Technol.*, 2011, **102**, 6742-6749.
5. T. R. Carlson, Y.-T. Cheng, J. Jae and G. W. Huber, *Energy & Environmental Science*, 2011, **4**, 145-161.
6. H. Zhang, T. R. Carlson, R. Xiao and G. W. Huber, *Green Chemistry*, 2012, **14**.
7. A. Aho, N. Kumar, A. V. Lashkul, K. Eränen, M. Ziolek, P. Decyk, T. Salmi, B. Holmbom, M. Hupa and D. Y. Murzin, *Fuel*, 2010, **89**, 1992-2000.
8. F. A. Agblevor, O. Mante, N. Abdoulmoumine and R. McClung, *Energy Fuels*, 2010, **24**, 4087-4089.
9. O. D. Mante, F. A. Agblevor and R. McClung, *Fuel*.
10. O. D. Mante, F. A. Agblevor, S. T. Oyama and R. McClung, *Bioresour. Technol.*, 2012, **111**, 482-490.
11. O. D. Mante, F. A. Agblevor, S. T. Oyama and R. McClung, *Applied Catalysis A: General*, 2012, **445–446**, 312-320.
12. Q. Lu, Z.-F. Zhang, C.-Q. Dong and X.-F. Zhu, *Energies*, 2010, **3**, 1805-1820.
13. D. Wang, R. Xiao, H. Zhang and G. He, *Journal of Analytical and Applied Pyrolysis*, 2010, **89**, 171-177.
14. H. Zhang, R. Xiao, H. Huang and G. Xiao, *Bioresour. Technol.*, 2009, **100**, 1428-1434.
15. D. J. Mihalcik, C. A. Mullen and A. A. Boateng, *Journal of Analytical and Applied Pyrolysis*, 2011, **92**, 224-232.
16. E. F. Iliopoulou, E. V. Antonakou, S. A. Karakoulia, I. A. Vasalos, A. A. Lappas and K. S. Triantafyllidis, *Chemical Engineering Journal*, 2007, **134**, 51-57.
17. S. Stephanidis, C. Nitsos, K. Kalogiannis, E. F. Iliopoulou, A. A. Lappas and K. S. Triantafyllidis, *Catalysis Today*, 2011, **167**, 37-45.
18. D. L. Compton, M. A. Jackson, D. J. Mihalcik, C. A. Mullen and A. A. Boateng, *Journal of Analytical and Applied Pyrolysis*, 2011, **90**, 174-181.
19. J. Jae, G. A. Tompsett, Y.-C. Lin, T. R. Carlson, J. Shen, T. Zhang, B. Yang, C. E. Wyman, W. C. Conner and G. W. Huber, *Energy & Environmental Science*, 2010, **3**, 358-365.
20. R. French and S. Czernik, *Fuel Processing Technology*, 2010, **91**, 25-32.
21. J. Adam, E. Antonakou, A. Lappas, M. Stöcker, M. H. Nilsen, A. Bouzga, J. E. Hustad and G. Øye, *Microporous and Mesoporous Materials*, 2006, **96**, 93-101.
22. P. T. Williams and N. Nugranad, *Energy*, 2000, **25**, 493-513.
23. S. Yorgun and Y. E. Simsek, *Bioresour. Technol.*, 2008, **99**, 8095-8100.
24. J. M. Encinar, J. F. González, G. Martínez and S. Román, *Journal of Analytical and Applied Pyrolysis*, 2009, **85**, 197-203.
25. E. Pütün, B. B. Uzun and A. E. Pütün, *Energy Fuels*, 2009, **23**, 2248-2258.
26. A. A. Boateng, C. A. Mullen and N. M. Goldberg, *Energy Fuels*, 2010, **24**, 6624-6632.
27. Catalytic pyrolysis of several kinds of bamboos over zeolite NaY W, http://chemistry.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.cfm?doi=b510602h&JournalCode=GC.
28. U.S. Department of Energy, Oak Ridge National Laboratory, Oak Ridge, TN. 227p., R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224., 2011.
29. S.-S. Kim, A. Shenoy and F. A. Agblevor, *Bioresour. Technol.*, 2014, **156**, 297-302.
30. O. D. Mante, J. A. Rodriguez and S. P. Babu, *Bioresour. Technol.*, 2013, **148**, 508-516.
31. S. Pan, Y. Pu, M. Foston and A. Ragauskas, *Bioenerg. Res.*, 2013, **6**, 24-34.

32.   P. F. Ffolliott, G. J. Gottfried and W. H. Kruse, *USDA Forest Service Proceedings*, 1999, **RMRS-P-9**, 254-259.

33.   DOE (U.S. Department of Energy), Department of Energy, Biomass Program, http://www.afdc.energy.gov/biomass/progs/search1.cgi, 2004.

34.   SGINC, *Composition of Herbaceous Biomass Feedstocks*, Prepared by North Central Sun Grant Center, SDSU, Brookings, SD 57007, 2007.

35.   T. E. Amidon, C. D. Wood, A. M. Shupe, Y. Wang, M. Graves and S. Liu, *Journal of Biobased Materials and Bioenergy*, 2008, **2**, 100-120.

36.   K. Wang, K. H. Kim and R. C. Brown, *Green Chemistry*, 2014, **16**, 727-735.

37.   A. G. Gayubo, A. T. Aguayo, A. Atutxa, R. Aguado and J. Bilbao, *Ind. Eng. Chem. Res.*, 2004, **43**, 2610-2618.

38.   A. G. Gayubo, A. T. Aguayo, A. Atutxa, R. Aguado, M. Olazar and J. Bilbao, *Ind. Eng. Chem. Res.*, 2004, **43**, 2619-2626.

39.   A. G. Gayubo, A. T. Aguayo, A. Atutxa, B. Valle and J. Bilbao, *Journal of Chemical Technology & Biotechnology*, 2005, **80**, 1244-1251.

40.   E. F. Iliopoulou, S. Stefanidis, K. Kalogiannis, A. C. Psarras, A. Delimitis, K. S. Triantafyllidis and A. A. Lappas, *Green Chemistry*, 2014, **16**, 662-674.

41.   J. Diebold and J. Scahill, in *Pyrolysis Oils from Biomass*, eds. E. J. Soltes and T. A. Milne, American Chemical Society, Washington, DC, 1988, pp. 264-276.

42.   C. D. Chang and A. J. Silvestri, *Journal of Catalysis*, 1977, **47**, 249-259.

43.   C. A. Mullen and A. A. Boateng, *Ind. Eng. Chem. Res.*, 2013, **52**, 17156-17161.

44.   F. A. Agblevor, S. Beis, O. Mante and N. Abdoulmoumine, *Ind. Eng. Chem. Res.*, 2010, **49**, 3533-3538.

45.   F. A. Agblevor, S. Besler and A. E. Wiselogel, *Fuel Science and Technology International ; VOL. 14 ; ISSUE: 4 ; Annual meeting of the American Institute of Chemical Engineers, San Francisco, CA (United States), 13-18 Nov 1994 ; PBD: 1996*, 1996, pp. 589-612 ; PL:.

46.   O. Mante, F. Agblevor and R. McClung, *Biomass Conversion and Biorefinery*, 2011, **1**, 189-201.

47.   A. Oasmaa, University of Jyväskylä, Finland, 2003.

48.   O. D. Mante and F. A. Agblevor, *Waste Management*, 2012, **32**, 67-76.

49.   F. A. Agblevor, O. Mante, R. McClung and S. T. Oyama, *Biomass and Bioenergy*, 2012, **45**, 130-137.

50.   F. de Miguel Mercader, M. J. Groeneveld, S. R. A. Kersten, N. W. J. Way, C. J. Schaverien and J. A. Hogendoorn, *Applied Catalysis B: Environmental*, 2010, **96**, 57-66.

51.   G. Fogassy, N. Thegarid, Y. Schuurman and C. Mirodatos, *Green Chemistry*, 2012, **14**, 1367-1371.

52.   N. Thegarid, G. Fogassy, Y. Schuurman, C. Mirodatos, S. Stefanidis, E. F. Iliopoulou, K. Kalogiannis and A. A. Lappas, *Applied Catalysis B: Environmental*, 2014, **145**, 161-166.

53.   M. S. Talmadge, R. M. Baldwin, M. J. Biddy, R. L. McCormick, G. T. Beckham, G. A. Ferguson, S. Czernik, K. A. Magrini-Bair, T. D. Foust, P. D. Metelski, C. Hetrick and M. R. Nimlos, *Green Chemistry*, 2014, **16**, 407-453.

54.   J. R. Keiser, M. A. Bestor, S. A. Lewis and J. Storey, Portland, OR, 2011.

55.   X. Fu, Z. Dai, S. Tian, J. Long, S. Hou and X. Wang, *Energy Fuels*, 2008, **22**, 1923-1929.

56.   S. Parkash, in *Refining Processes Handbook*, ed. S. Parkash, Gulf Professional Publishing, Burlington, 2003, pp. 109-152.

57.   M. T. Ghannam, S. W. Hasan, B. Abu-Jdayil and N. Esmail, *Journal of Petroleum Science and Engineering*, 2012, **81**, 122-128.

58.   S. W. Hasan, M. T. Ghannam and N. Esmail, *Fuel*, 2010, **89**, 1095-1100.

59.   R. Martínez-Palou, M. d. L. Mosqueira, B. Zapata-Rendón, E. Mar-Juárez, C. Bernal-Huicochea, J. de la Cruz Clavel-López and J. Aburto, *Journal of Petroleum Science and Engineering*, 2011, **75**, 274-282.
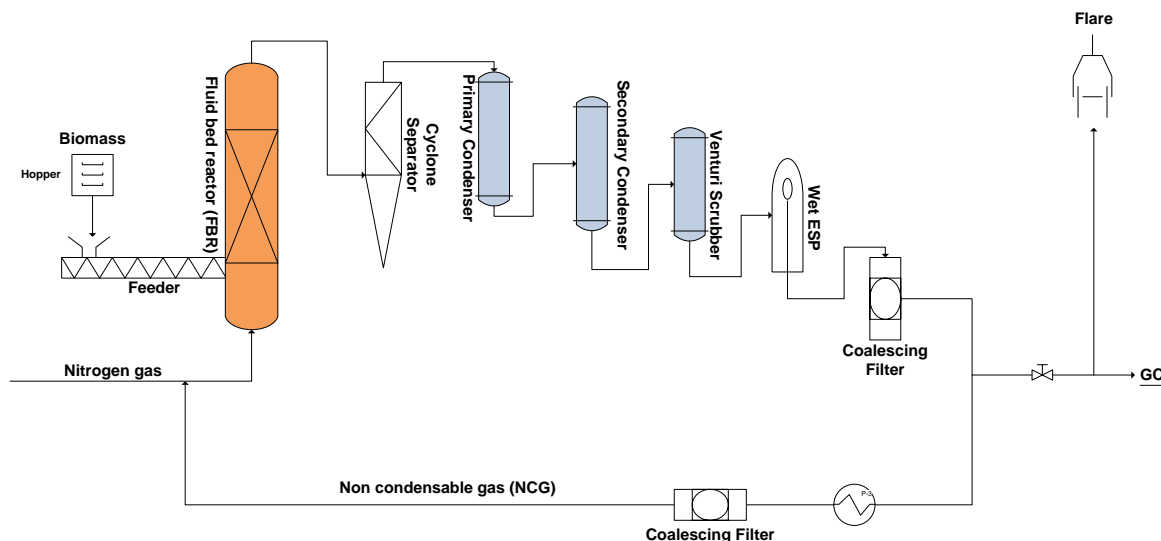
List of Figures

Figure 1a. Simplified Schematic diagram of the 2 kg/h pilot scale pyrolysis unit
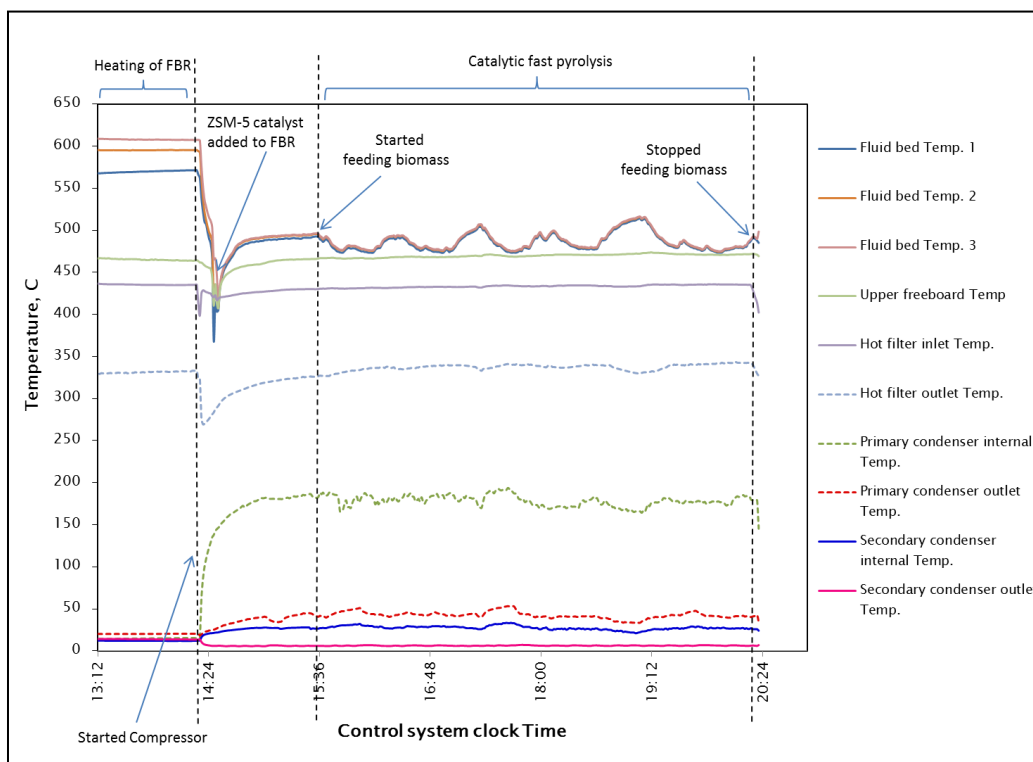

Figure 1b. Typical process temperature profile

28
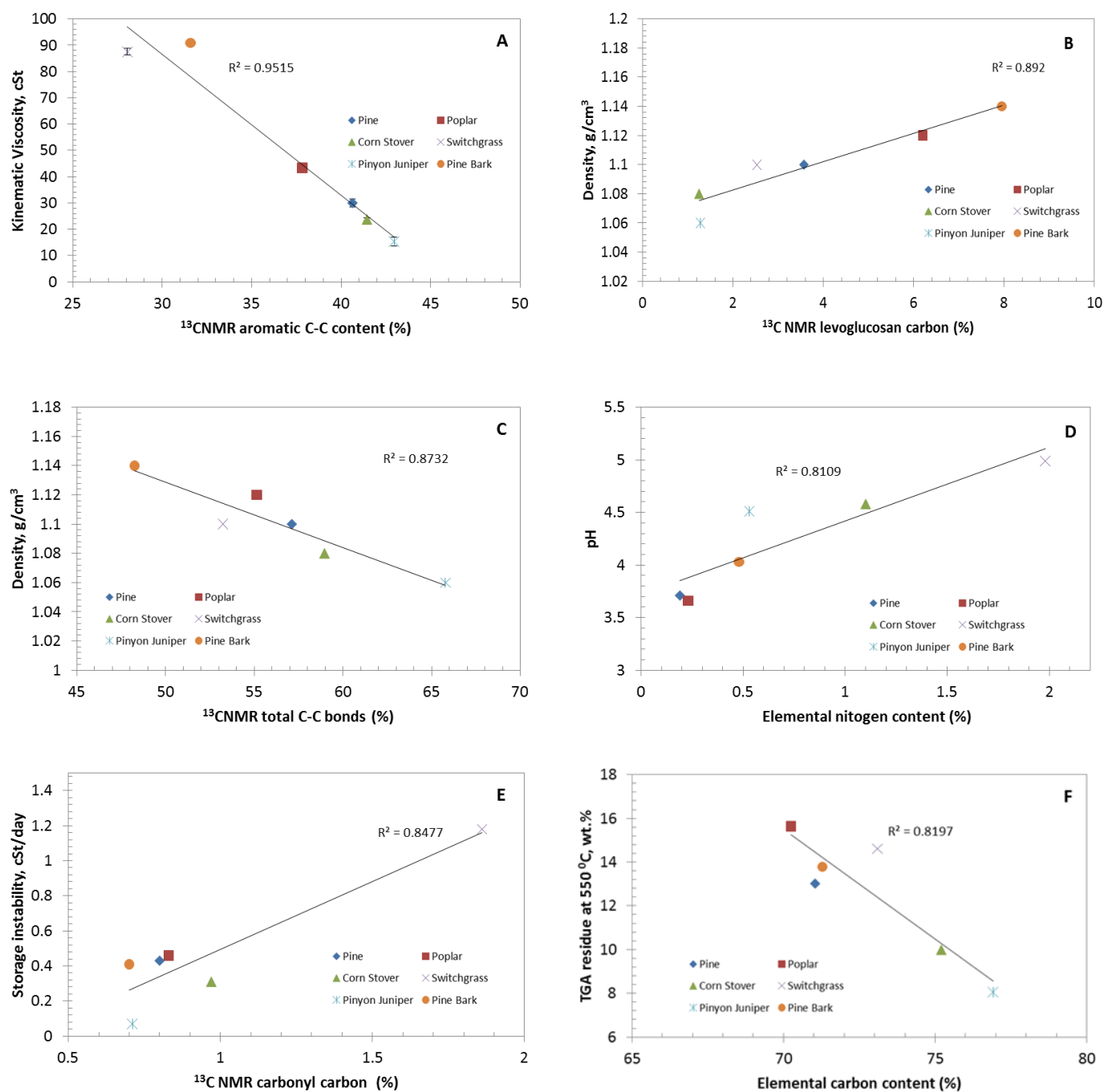
Figure 2. Correlation plots showing the relationship between the chemical composition of the biocrude oils and selected physical properties: (A) correlation between kinematic viscosity and aromatic C-C bonds; (B) correlation between levoglucosan carbons and density; (C) correlation between total C-C bonds and density; (D) correlation between elemental nitrogen content and pH; (E) correlation between carbonyl carbon and storage stability; (F) correlation between organic carbon content and TGA solid residue.

List of Tables

Table 1. GCMS product distribution of selected compounds from the catalytic pyrolysis of the biomass feedstocks at 550 ^{o}C and C/F ratio of 10 (w/w)

Quantified Compounds	Carbon Yields (%)					
	Hybrid Poplar	Pine	Pinyon-Juniper	Switchgrass	Corn Stover	Pine Bark
Monoaromatics						
Benzene	0.67	1.56	1.61	1.16	1.32	0.88
Toluene	1.44	1.97	2.22	1.87	2.11	1.75
Ethylbenzene	0.95	1.30	1.46	1.25	1.33	1.04
Xylene	3.03	4.29	4.75	4.09	4.28	3.34
Alkylbenzenes	5.14	8.59	7.34	6.66	6.51	5.55
Total	*11.2±0.3*	*17.7±0.5*	*17.4±0.4*	*15.0±0.3*	*15.5±0.3*	*12.6±0.1*
Oxygenates						
Methanol	0.07	0.13	0.09	0.12	0.11	0.02
Acetic Acid	0.33	0.41	0.27	0.52	0.90	−
2-methyl phenol	0.03	0.09	0.06	0.09	0.06	0.01
4-methyl phenol	0.05	0.14	0.10	0.15	0.10	0.02
3-ethyl phenol	0.13	−	−	0.11	0.03	0.04
Dimethyl phenol	0.03	0.11	0.07	0.10	0.04	−
Total	*0.64*	*0.88*	*0.59*	*1.09*	*1.24*	*0.09*

Other aromatic hydrocarbons such as naphthalenes, indenes, indane, and PAHs were identified but not quantified.

Table 2. Product yields (wt% on biomass) and gas composition of the product gas from the pilot-scale catalytic pyrolysis with ZSM-5 zeolite

Pyrolysis Product	Yields (wt %)					
	Hybrid Poplar	Pine	Pinyon-Juniper	Switchgrass	Corn Stover[+]	Pine Bark[+]
Total liquid product	41.1±4.2	42.5±2.5	39.2±0.3	40.3±4.2	36.8	34.8
WESP fraction	8.4±2.8	9.3±1.5	10.2±1.1	10.0±2.6	5.3	6.4
Condenser fraction	32.7±1.4	32.2±4.0	29.2±1.1	30.2±1.6	31.5	37.6
Char/coke	17.0±1.6	17.5±3.6	22.8±0.5	25.0±0.8	26.45	33.4
Gases (by difference)	41.9±5.7	40.0±1.1	38.0±0.6	34.7±5.0	36.8	31.8
*Gas composition (mol %, N_2 free basis)						
H_2	4.3±0.7	4.7±1.3	3.8±1.4	3.9±1.1	3.3	3.0
CO	53.8±0.6	55.2±1.3	48.9±1.2	42.0±0.9	47.2	50.8
CO_2	28.7±0.9	27.0±1.3	29.1±1.8	39.4±0.7	35.9	33.5
CH_4	6.1±1.1	6.3±1.5	7.6±1.8	8.4±1.9	5.9	5.2
C_2-C_5	7.0±0.9	6.8±1.1	10.5±1.3	6.3±1.3	7.8	7.6
CO/CO_2	1.9±0.1	2.0±0.1	1.7±0.1	1.2±0.1	1.3	1.5

+The yields are based on two runs.* Average composition of the product gas sampled after the coalescing filter at time interval of 3.25 mins during recycling of the gases in catalytic pyrolysis experiment.

Table 3. Physicochemical properties of the biocrude oils produced from all six biomass sources

	Biocrude oils					
Property	Pine	Hybrid poplar	Corn Stover	Switchgrass	Pinyon juniper	Pine Bark
Elemental, wt.% (dry basis)						
C	74.12	73.28	78.46	76.23	80.24	74.37
H	6.26	6.23	6.40	6.98	6.92	6.26
O*	19.42	20.25	13.99	14.72	12.29	18.87
N	0.20	0.24	1.15	2.07	0.55	0.5
S	BDL	BDL	BDL	BDL	BDL	BDL
H/C molar ratio	1.01	1.02	0.98	1.10	1.03	1.01
O/C molar ratio	0.20	0.21	0.13	0.14	0.11	0.19
Physical properties						
pH	3.71	3.66	4.58	4.99	4.51	4.03
Density (g/cm^3)	1.10	1.12	1.08	1.10	1.06	1.14
Estimated gravity, ^{o}API	-2.9	-5.2	-0.5	-2.9	2.0	-7.4
Kinematic Viscosity (at 40 ^{o}C, cSt)	30.0	43.3	23.7	87.5	15.3	90.9
Dynamic Viscosity (at 40 ^{o}C, cP)	33.2	48.6	25.6	95.9	16.2	103.5
Long term storage Stability (Viscosity after 12 months of storage, at 40 ^{o}C, cSt)	206.3	217.5	140.9	536.1	41.0	247.6
Average rate of viscosity change,(cSt/day)	0.43	0.46	0.31	1.18	0.07	0.41
TGA amount degraded below 400 ^{o}C, wt.%	83.95	81.16	87.47	81.46	89.96	83.16
TGA residue at 550 ^{o}C, wt.%	13.02	15.63	9.99	14.61	8.06	13.79

BDL = below detection limit

32