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Reforming Biomass Derived Pyrolysis Bio-oil Aqueous Phase to Fuels

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Abstract

Fast pyrolysis and catalytic fast pyrolysis (CFP) of biomass produce a liquid product stream comprised of various classes of organic compounds having different molecule size and polarity. This liquid, either spontaneously in the case of catalytic fast pyrolysis or by water addition for the non-catalytic process separates into a non-polar organic-rich fraction and a highly polar water-rich fraction. The organic fraction can be used as a blendstock or feedstock for further processing in a refinery while, in the CFP process design, the aqueous phase is currently sent to wastewater treatment, which results in a loss of residual biogenic carbon present in this stream. This work focuses on the catalytic conversion of the biogenic carbon in pyrolysis aqueous phase streams to produce hydrocarbons using a vertical micro-reactor coupled to a molecular beam mass spectrometer (MBMS). The MBMS provides real-time analysis of products while also tracking catalyst deactivation. The catalyst used in this work was HZSM-5, which upgraded the oxygenated organics in the aqueous fraction from non-catalytic fast pyrolysis of oak wood to fuels comprising small olefins and aromatic hydrocarbons. During processing the aqueous bio-oil fraction the HZSM-5 catalyst exhibited higher activity and coke resistance than those observed in similar experiments using biomass or whole bio-oils. Reduced coking is likely due to ejection of coke precursors from the catalyst pores that was enhanced by excess process water available for steam stripping. The water reacted with coke precursors to form phenol, methylated phenols, naphthol, and methylated naphthols. Conversion data shows that up to 40 wt% of the carbon in the feed stream is recovered as hydrocarbons.

Keywords: Bio-oil aqueous fraction, upgrading, HZSM-5, steam stripping, hydrocarbon fuels, phenols

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1. INTRODUCTION

The conversion of lignocellulosic biomass into hydrocarbon fuels has garnered interest from governments, industry and the scientific community. This renewable resource is abundant worldwide and can potentially produce transportation fuels that are less harmful to the environment compared to fossil fuels. Fast pyrolysis is an attractive thermochemical technology for converting biomass into precursors for hydrocarbon fuels because it produces up to 75 wt% bio-oil.[1] This bio-oil is composed of over 300 oxygenated organic compounds, that are thermal degradation products of three major biomass building polymers; cellulose, hemicellulose, and lignin. Despite different polarity of various groups of those compounds bio-oil is usually a single-phase liquid. However, addition of water to bio-oil results in a phase separation with the larger and less polar, mostly lignin-derived molecules forming a very viscous bottom fraction, while the more polar compounds originating from cellulose and hemicellulose migrate to the top aqueous phase. While much research has focused on converting the organic phase to hydrocarbon fuels, little work has been done to utilize the aqueous fraction, which can contain up to 60 % of the original biomass carbon.[2] Investigation of the conversion of organics in the aqueous phase can improve the feasibility of a biorefinery in two ways; first the organics in the aqueous phase will have limited amounts of lignin pyrolysis products, which are known potent coke precursors and catalyst fouling agents,[3-5] and second, this approach will help develop technology for valorizing carbon contained in aqueous waste streams offsetting water treatment costs in biorefineries while sustainably processing the carbon to fuels and chemicals.

Early studies used zeolites, especially HZSM-5, to upgrade model compounds found in the aqueous phase of bio-oil such as propanoic acid, acetic acid, methyl esters, 4-ethyl cyclohexanol and cyclopentanone.[6-7] These studies revealed how upgrading these species using HZSM-5 consisted of complex reaction mechanisms involving cracking, deoxygenation, aromatization and polymerization, which formed aromatic hydrocarbons and also resulted in severe catalyst coking. Other studies investigated upgrading acetic acid, alcohols, acetaldehyde and ketones over HZSM-5 and found that alcohols, ketones and acetic acid produced olefins and aromatic hydrocarbons whereas aldehydes were unreactive.[3, 8] This was attributed to high coking rates for acetaldehydes compared to alcohols, acetic acid and ketones. Another group upgraded synthetic bio-oil composed of acetic acid, 2-furaldehyde, cyclohexanone, guaiacol, vanillin and water using HZSM-5, FCC, Fe/Cr, alumina and Al-MCM-41 catalysts.[9] They found that HZSM-5 completely deoxygenated species in the synthetic bio-oil to form aromatic hydrocarbons while the Fe/Cr transition metal catalyst formed phenol and alkyl phenols. In a recent study, various aqueous feed mixtures comprising ethanol, ethanol + acetic acid, ethanol + ethyl acetate, or ethanol + acetaldehyde were processed using HZSM-5 in a fixed bed reactor.[10] This work showed that those additions to ethanol resulted in reduced catalyst lifetimes and analysis of the spent catalyst revealed that the presence of acetaldehyde appeared to produce high molecular weight aromatic compounds which deactivated the catalyst by blocking its pores. This study also suggested that each functional group of oxygenates required a different active site for conversion to desired products and thus, it was necessary to upgrade the mixture of oxygenates to produce a feed stream containing the same functional group of compounds before upgrading over HZSM-5.

There has been some progress in processing actual aqueous bio-oil fractions using HZSM-5.[11-17] Gayubo et al[11] using HZSM-5 converted pine bio-oil fraction to olefins (mostly propylene and ethylene) and aromatic hydrocarbons. At 500 °C and weight hourly space velocity (WHSV) of 4.2 the initial yields were respectively 42 % and 22 % then rapidly decreased with time-on-stream due to the catalyst deactivation resulting mostly from coke deposition (9.5% of the feed carbon). They found that the deactivation by coke was reversible and is similar to the deactivation from upgrading model compounds.[3, 8] However, another form of deactivation occurred caused by dealumination due to excess steam in the feed.

This deactivation by dealumination occurred at 450°C and was irreversible because it resulted in deterioration of the total acidity of the catalyst. Using HZSM-5 for conversion of pine bio-oil aqueous fraction at 600°C and WHSV of 11.7 Vispute et al[13] produced aromatic hydrocarbons with a yield of 8.2 % and olefins at 18.5 % while 32 % of the carbon in the feedstock was converted to coke. Higher yields of olefins and aromatic hydrocarbons were obtained when the aqueous fraction was first partly hydrogenated using Ru/C and Pt/C catalysts that resulted in the reduction of carbonyl groups to hydroxyls.[13-14]

In this study, we investigated the catalytic upgrading of the bio-oil aqueous phase to form fuels or fuel precursors. We observed changes in the product distribution as a function of the catalyst time on stream, which will help optimize the process conditions, specifically the catalyst residence time in the reactor, for the production of hydrocarbons. We performed two different but complementary experiments using reactors coupled with; 1) a molecular beam mass spectrometer (MBMS) and 2) a gas chromatograph mass spectrometer (GCMS) to measure and assess product formation. In the MBMS experiment the aqueous oil fraction was continuously fed through an ultrasonic nebulizer using a syringe pump into a reactor containing a fixed bed of catalyst. This configuration provides real-time measurement of the composition of the upgraded products while also tracking catalyst deactivation by product composition changes. The identity of the upgraded products was confirmed using GCMS in a separate on-line experiment. The catalyst used in this study was HZSM-5, which is known to deoxygenate bio-oils and biomass via dehydration, decarboxylation, and decarbonylation reactions to produce olefins and aromatic hydrocarbons.[18-22]

2. MATERIALS AND METHODS

Experiments were primarily conducted using the MBMS system; this apparatus allows for continuous feeding of the aqueous oil and real-time measurements of the products formed during the catalytic upgrading process. In addition, experiments were conducted with the GCMS to identify some products. Coke on spent catalyst was measured using thermogravimetric analysis (TGA). The number of acid sites on fresh and spent catalyst samples was measured with NH_3 temperature-programmed desorption (TPD).

2.1. Materials. The aqueous phase oil was generated at NREL using the method described below. The catalyst was a Johnson Matthey HZSM-5 with the silica to alumina ratio (SAR) of 30 supported on a silica binder used previously with whole biomass.[23]

2.2. Aqueous Oil Preparation. The aqueous fraction was produced from oak pyrolysis oil made in the NREL pilot scale system by pyrolyzing 2 mm oak particles at 500°C in an entrained flow reactor with a nitrogen carrier gas. The bio-oil was condensed by spray quenching with cold dodecane and collected as the bottom fraction immiscible with hydrocarbons. The bio-oil was then mixed with an equal weight of water and stirred for six hours with a paddle stirrer and stationary baffle to enhance remixing of the very viscous organic phase with the more fluid aqueous phase. The mixture was allowed to phase separate for 48 hours before the aqueous phase was decanted off. The aqueous phase included 70 wt% of water, as determined by Karl-Fisher titration; organic content was estimated at 30 % by difference. A 2D GCMS was used to characterize volatile parts of both whole oil and its aqueous fraction.

2.3. Catalytic upgrading with the MBMS Reactor System. The catalytic upgrading of the organic species in the aqueous phase was performed in a vertical reactor system using a fixed bed containing one-gram of catalyst. The schematic of this reactor system is shown in Figure S1 (supplementary information) and has been described previously.[4, 24-25] The aqueous fraction was introduced into the reactor using a syringe pump and an ultrasonic nebulizer. The nebulizer produced aerosol from the liquid that was partly non-volatile (carbohydrates) and would otherwise deposit in the evaporator or the reactor freeboard. The ultrasonic feed system was initially evaluated and optimized at

conditions that allow it to deliver consistent feed stream to the catalyst bed. The reactor temperature and nebulizer nozzle power settings were optimized to 500 ^{o}C and 4 watts respectively. The vertical reactor system consists of a quartz microreactor with two He inlet ports. Helium was introduced through one of the inlets at a flow rate of 400 sccm to entrain the feed stream. In addition to entraining volatile components of the aqueous phase, He gas was also used as a sweeping gas to quench secondary reactions by dilution at the exit of the reaction zone and prior to the MBMS. The flow rate of the diluent He was 4000 sccm. The quartz microreactor was housed in a tube furnace with five zones independently controlled and heated to 500 °C before beginning the experiment.

The catalyst was loaded into the reactor tube (I.D. = 7.5 mm) resulting in a catalyst bed volume of approximately 1.0 cc. At the carrier gas flow rate of approximately 400 sccm, the residence time of the feed stream in the catalyst bed was approximately 0.06 s at 500 °C. Typically, an experimental run consisted of continuously feeding the aqueous bio-oil fraction at a rate of approximately 3 gh^{-1}. In these experiments, the weight hourly space velocity based on the organic material (30 % of the feed) was approximately 1 h^{-1}.

The experiments were carried out with the reactor interfaced directly to the MBMS for real-time product analysis. The diluent He carried the upgraded vapors into the source of the mass spectrometer with minimal condensation or additional thermal cracking on the hot reactor surfaces. The MBMS system[4, 23-31] is well suited for real time sampling of high-temperature condensable vapors formed during pyrolysis and/or catalytic fast pyrolysis of biomass. In this system, the produced vapors and gases undergoes rapid, adiabatic expansion through a 250 μm orifice into a vacuum chamber held at ~ 100 mtorr. This expansion cools the gas and effectively freezes the chemistry occurring in the reactor and improves the sensitivity of the instrument. Further, cooling the gas helps minimize fragmentation during ionization and improves mass spectral signals. The cooled gas is skimmed into a molecular beam as it is drawn into another vacuum stage. This molecular beam is then ionized with an electron impact ionization source (22.5 eV) of a quadrupole mass spectrometer, yielding positive ions. The MBMS was set to measure over the m/z 10-500 amu with the scan rate of about 1.0ms/amu. This instrument has the advantage of near universal detection and can measure signals for a wide variety of molecular species from the catalytic reforming of biomass. In the micro-reactor experiments, a small, precisely controlled flow of argon (40 sccm) mixed with helium carrier gas passing inside the micro-reactor is used as a tracer gas. Argon appeared on the MBMS spectra as m/z 40 and was thus used to normalize the concentrations of other gases and vapors produced and measured on the MBMS. This allows us to compare relative concentrations between experimental conditions to minimize errors in quantifying the products.

To quantify products, an eight-component liquid calibration standard containing benzene, toluene, *m*-xylene, indene, naphthalene, methylnaphthalene, 1,3-dimethynaphthalene and phenanthrene (AccuStandard) and a six-component gas standard containing butene, carbon dioxide, carbon monoxide, ethylene, helium and propylene (Air Liquide) were run through the reactor at three different concentrations. The resulting calibration curves were used to calibrate these components directly and the range of sensitivity factors measured on the 14 components were used to estimate ranges of the amounts of the other products seen.

2.4. GCMS System. The products obtained from MBMS system were identified and validated by GCMS. The schematic of the GCMS is depicted in Figure S2 and a detailed description of this reactor system was discussed previously.[23, 29, 31-32] Briefly, the micropyrolyzer (Rx-3050TR, Frontier Laboratories, Japan) has two heating zones, one for volatilizing the aqueous phase and a downstream zone for catalytic upgrading. The system is equipped with a microjet cryo-trap (MJT-1030Ex) coupled to the GCMS, for identifying the upgraded products. About one microliter samples of the aqueous oil loaded in a syringe were directly injected in the volatilizing reactor set to 500 °C. The volatile components of the aqueous oil were entrained in He and transported through a 20 mg fixed catalyst bed (also set to 500 °C) for

upgrading. The upgraded vapors were subsequently captured using a liquid nitrogen trap (set to -196 ^{o}C, housed inside the GC oven) and desorbed into the inlet of the gas chromatograph (7890B, Agilent Technologies, USA) interfaced with the MS (5977A, Agilent Technologies, USA). The trapped gases were separated by a capillary column (Ultra Alloy-5, Frontier Laboratories, Japan) with a 5 % diphenyl and 95 % dimethylpolysiloxane stationary phase. The oven was programmed to hold at 40 °C for 3 min followed by heating to 300 °C at the ramp rate of 10 °C/min. Products recorded on the mass spectrometer were identified using standards and NIST GCMS library. [23, 29, 32]

3. RESULTS AND DISCUSSION

3.1. Characterization of the Aqueous Fraction of Bio-oil. Volatile species in the aqueous oil were identified using 2D-GCMS. Table 1 shows the difference between the composition of whole bio-oil and aqueous oil. It includes only the most abundant components; the more complete list can be found in a recent study.[33] The aqueous bio-oil fraction consists of aldehydes, ketones, organic acids, and levoglucosan, which are produced from the carbohydrate component of biomass as reported in numerous previous publications.[1, 13, 34-41] Most of the species in the aqueous bio-oil fraction have a short carbon chain backbone but they all contain oxygen. Some of the oxygen containing functional groups are responsible for undesired properties of bio-oil, for example acetic acid results in high acidity and aldehydes and ketones cause the bio-oil instability. A significant part of the aqueous bio-oil fraction components has not been identified and quantified because it did not volatilize in the GC injector. Most likely those components are polyols formed from thermal degradation of cellulose and hemicellulose.

3.2. Upgrading the Aqueous Oil Fraction. Upgrading the organics in the aqueous fraction over HZSM-5 resulted in formation of olefins and aromatic hydrocarbons. The excess water in this fraction redirected some of the polyaromatic hydrocarbons to formation of phenol, cresols and naphthols. Figure 1 shows the mass spectrum of raw aqueous bio-oil fraction recorded when the aqueous bio-oil fraction was introduced in the 500 ^{o}C heated vertical reactor with inert material (sand) used as the catalyst bed. The species in the aqueous bio-oil fraction consists of mainly cellulose and hemicellulose derived compounds; levoglucosan m/z 162, 1,4:3,6-dianhydro-α-D-glucopyranose m/z 144 (also a fragment ion of levoglucosan), 5-hydroxymethyl furfural or levoglucosenone m/z 126, catechol m/z 110, furfuryl alcohol m/z 98, and some low molecular weight species (acetic acid and hydroxyacetaldehyde m/z 60). The peaks at m/z 55, 57 and 73 are typical fragment ions from carbohydrate pyrolysis products and the peak at m/z 43 is usually observed in the presence of carbonyl compounds such as hydroxy-propanone.[4, 36, 400] The peaks at m/z 69, 97 and 110 are fragment ions of 5HMF and the peaks at m/z 31 and 32 are fragment ions of hydroxyacetaldehyde.[30] This result agrees well with the species identified in the aqueous bio-oil fraction using the 2D-GCMS set-up. Note that the MBMS spectrum also contains less intense high molecular weight weak peaks that could be derived from sugar oligomers and/or the lignin component, for example guaiacol m/z 124.[13]

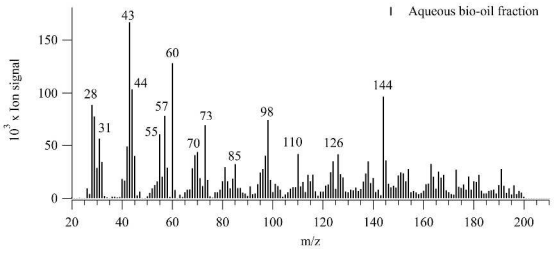

Figure 1. The mass spectrum of raw aqueous bio-oil fraction recorded using molecular beam mass spectrometry. Reaction conditions: Aqueous fraction vapor volatilization at 500 °C, 1 atm, WHSV ~ 1 h^{-1}, 1.0 g sand.

Figure 2 shows mass spectra recorded at 10 minute intervals during upgrading of the aqueous fraction with HZSM-5 at 500 °C. Figure 2A shows that upgrading the aqueous bio-oil with fresh HZSM-5 results in almost complete deoxygenation of these species to form olefins and aromatic hydrocarbons. The olefins

formed include ethylene m/z 28 (also due to CO), and propylene m/z 42. The aromatic hydrocarbons formed include benzene and alkylated benzenes (m/z 78, 92, 106 and 120), indene m/z 116, indane m/z 118, naphthalene and alkylated naphthalenes (m/z 128, 142 and 156), and anthracene and alkylated anthracenes (m/z 178, 192 and 206).[4, 20, 42-44] Oxygen was rejected as H_2O m/z 18, CO m/z 28 (also due to ethylene) and CO_2 m/z 44. These assignments were confirmed with py-GCMS studies discussed below. Similar deoxygenated products were also observed when biomass materials or whole bio-oils were upgraded over HZSM-5 at 500 °C.[45-49] Figure 2A also show weak peaks for oxygenated products (highlighted in red) for phenol and alkyl phenols (m/z 94 and 108) and naphthol and alkyl naphthol (m/z 144 and 158). These oxygenated species are formed from the reactions of steam with aromatic precursors in zeolite pores as reported previously during catalytic fast pyrolysis of biomass with HZSM-5 in the presence of added steam.[23] The observation of these oxygenates did not indicate that the catalyst had deactivated since they were formed from side reactions. The mass spectrum in Figure 2B shows formation of additional peaks for furan m/z 68 and methyl furan or cyclopentenone m/z 82 (highlighted in blue), indicating that the catalyst was starting to deactivate after 10-20 minutes time on stream (after processing the amount of feed equal to 0.5-1 times of its weight). Furans are partially deoxygenated products formed in zeolites from the carbohydrate component of biomass.[4, 20, 42, 50-51] The intensities of these oxygenated products increased with time on stream as shown in Figure 2C, and additional oxygenated peaks, for example catechol m/z 110, are observed in the mass spectrum, indicating catalyst deactivation (after processing the amount of feed about 1.5 times its weight).

To further explore catalyst deactivation, we monitored how the upgraded products shown in Figure 2 changed with time as more aqueous bio-oil was fed through the fixed bed. Figure 3 shows the ion counts of representative model compounds for one-ring (benzenes), two-ring (naphthalenes), and three-ring (anthracenes) aromatic hydrocarbons, phenols (including naphthols), furan intermediates, catechols and furfuryl alcohol. At the start of the experiment, fresh HZSM-5 upgrades the aqueous bio-oil to form one and two -ring aromatics and the three-ring aromatics appear to form after a small induction period. The delay in appearance of the three-ring aromatics in the mass spectrum could be related to their kinetic diameters, since the more compact molecules easily escape from the pores of the catalyst compared to the less compact bulkier molecules. It appears that the one-ring and two-ring aromatics are formed at the same time, which is different from what was observed during studies conducted with pulses of biomass during catalyst fast pyrolysis using the same HZSM-5 sample, where the two-ring aromatics appeared at a later time compared to one-ring aromatics due to their low kinetic mobility inside the pores of the catalyst.[23] This could be because the excess water from the bio-oil pushes the two ring aromatics so that they exit the pores of catalyst at the same time as one-ring aromatics.

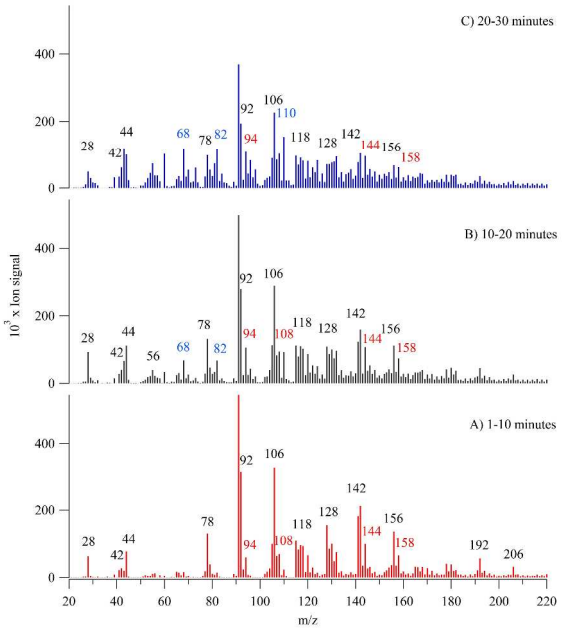

Figure 2. Mass spectra recorded from upgrading volatile components of the aqueous fraction of pine bio-oil shown in Figure 1 over a fixed bed of HZSM-5 a) first 10 minutes, B) second 10 minutes, and C) third 10 minutes. Reaction conditions: Aqueous fraction vapor upgrading at 500 °C, 1 atm, WHSV ~ 1 h^{-1}, 1.0 g catalyst.

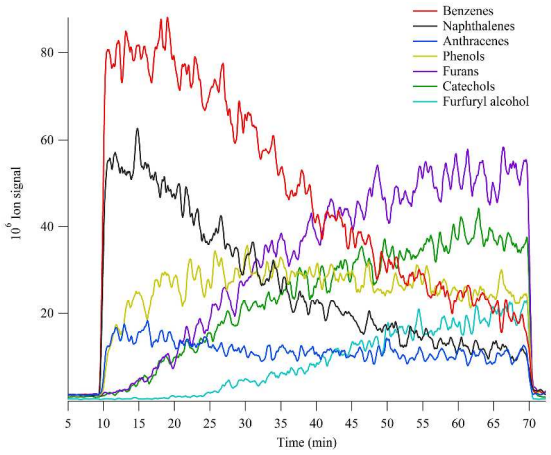

Figure 3. Ion count profiles of species produced from upgrading the aqueous bio-oil fraction using HZSM-5 as a function of time on stream. Reaction conditions: Aqueous fraction vapor upgrading at 500 °C, 1 atm, WHSV ~ 1 h^{-1}, 1.0 g catalyst.

The formation of the three-ring aromatics is usually accompanied by coke formation,[4, 23, 29] which quickly deactivates the catalyst. In this study, the catalyst remained active towards formation of one-ring aromatics for approximately 30 minutes after these species have been formed. This prolonged activity of HZSM-5 could be attributed to the excess water in the aqueous fraction reacting with coke precursors (polyaromatics) to form one-ring aromatics, phenols and naphthols. Similar results were observed during catalytic fast pyrolysis of biomass with HZSM-5 in the presence of added steam.[23] Water can also compete with organic species for adsorption sites on the catalyst surface, reducing rate of coke formation. Figure 3 also shows that the amount of one-ring aromatic hydrocarbons formed from time 10 to 25 minutes is almost constant, whereas the two-ring aromatic hydrocarbons decrease. Water in the cages of zeolites was previously demonstrated to have a steric effect on the adsorbate/ intermediate, which impacted ethylene to propylene selectivity during methanol-to-olefin conversion.[52] This could help explain the observed product selectivity between benzenes and naphthalenes in the first 15 minutes.

Figure 3 also shows the ion counts for phenols and naphthols, which were not observed in the raw aqueous bio-oil fraction in Figure 1. As can be seen in Figure 3, these species were formed after a small induction period and continued to increase in concentration during the experiment. The phenols and naphthols were not observed this early in biomass CFP studies conducted without water,[4] however they were observed early during catalytic fast pyrolysis of biomass with added steam.[23] In the current experiment, these species are observed immediately after the three-ring aromatics. In addition to being formed from the reaction of steam with aromatic precursors in zeolite, they could also be formed through steam stripping of coke from the HZSM-5 catalyst.[23] Steam stripping can also form some aromatic hydrocarbons.[23]

The ion signal for aromatic hydrocarbons decrease with time as more aqueous oil is fed through the bed but the phenols and naphthols increase. This implies that more coke precursors are being formed in the pores, which will decrease the activity of the catalyst as shown by formation of another group of oxygenated species (furan intermediates and catechol) starting at approximately t = 15 minutes. Coke formation could also occur through deposition of the non-volatile species present in the aqueous oil on the catalyst surface. The catalyst is deactivated when the primary volatilization products (Figure 1) start breaking through the catalyst without reacting. For example, furfuryl alcohol m/z 98, forms at time t = 25 minutes in Figure 3 and increases gradually for the remainder of the experiment. The decrease in activity of the catalyst can be observed in Figure 4, which shows the mass spectra recorded during the last 30 minutes of the experiment. Compared to the mass spectra in Figure 2, Figure 4A shows the shift in product distribution to a few one-ring aromatics, partially deoxygenated products (furan intermediates), side products (phenols and naphthols) and primary volatilization products (Figure 1). The mass spectrum in Figure 4B shows a decrease in deoxygenated products and an increase in oxygenated products. Towards the end of the experiment the mass spectra in Figure 4C looks similar to Figure 1, indicating severe

catalyst deactivation. The observation of furan intermediates in Figure 4C indicates that the catalyst might still have accessible active sites.

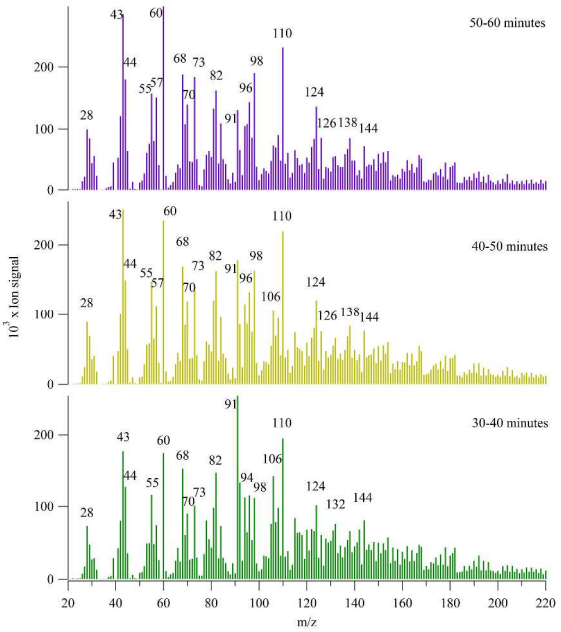

Fig. 4. Spectrum recorded during the last 30 minutes of upgrading the aqueous bio-oil fraction using HZSM-5. Reaction conditions: Aqueous fraction vapor upgrading at 500 °C, 1 atm, WHSV ~ 1 h^{-1}, 1.0 g catalyst.

Based on the calibration the yields were calculated for 10 minute intervals over the first 30 minutes of the test. The results are shown in Table 2. The feedstock carbon to aromatic hydrocarbons and olefins conversion in the first 30 minutes ranged from 32-40 %, which is not as high as reported by Gayubo[9] but better than obtained by Vispute[10]. The alkenes and aromatic hydrocarbons were the major products at the beginning of the run with around 40 % carbon yield. The yield of hydrocarbons decreased over time due to formation of other species (furans, phenols and naphthols) as shown in Figure 3. The mass balances are less than 100 % because we did not account for char (polymerized carbon on the reactor walls) and catalyst coking. Towards the end of the experiment, the products are dominated by unconverted volatilization oxygenates as shown in Figure 4 so it is challenging to accurately calculate the yields of olefins and aromatics, since some will have similar nominal molecular weights.

The CO and CO_2 are higher than possible since it would account for more oxygen than was present in the feedstock. The m/z 28 signal used for CO was corrected for ethylene based on fragment ions, but m/z 44 used for CO_2 was not corrected for contribution from propane. The water content was also not as expected – it was less than the water estimated in the feedstock and it is expected that water will be produced on the catalyst from oxygenates. Although it seems unlikely at 500 ^{o}C, we are considering the possibility that the excess steam that is being fed is converting a fraction of the coke or its precursors to CO and CO_2 driven by the mass action of excess steam. Hence, three factors may improve the conversion of the aqueous phase compared to whole oils or biomass vapors: reduced carbon precursor formation, steam stripping of coke precursors from the catalyst, and the gasification of the fresh carbon to carbon oxides.

3.2. Catalyst Characterization. Spent HZSM-5 samples were collected after 10, 20 and 60 minutes time on stream and analyzed using thermogravimetric analysis (TGA), ammonia TPD and ^{27}Al solid state NMR and the results were compared with those of a fresh HZSM-5 sample. The TGA results of the spent catalysts in Figure S3 (supplementary information), show two mass loss regions at low temperature (100-250 ^{o}C) and at high temperature (500-700 ^{o}C). The mass loss at low temperature is attributed to the moisture adsorbed in the catalyst pores after the experiment. The moisture on the catalyst is adsorbed from the room during the catalyst shelf life after the experiment is completed. As can be seen, coked catalysts adsorb less moisture compared to the fresh catalyst because of pore blocking from the coke. For the coked catalysts, the amount of moisture adsorbed decreases with increasing time on stream because of increase in the amount of coke deposited on the catalysts. The mass loss at high temperature is attributed to the amount of coke deposited on the catalyst. The amounts of coke deposited on the catalysts are very low (0.5-0.9 %) compared to those reported in literature[9, 10] for similar processes, which may be due to lower space velocity used in our tests. The coke amounts are also lower than those observed in catalytic fast pyrolysis of

biomass and the whole bio-oil. This could be because of the excess water, which has been shown to reduce catalyst coking and also different composition of species in the aqueous fraction. Real biomass and bio-oils also contain lignin monomers and oligomers, which can easily form coke both on the exterior surface and inside the pores.

Additional tests (^{27}Al NMR and NH_3-TPD) were conducted to investigate the effect of the excess steam on HZSM-5 dealumination of the three spent catalysts. ^{27}Al solid state NMR spectroscopy was used for determining framework and extra framework Al content of zeolites. Figure S4 show results from solid state NMR conducted on the same spent HZSM-5 samples. As can be seen, there is no significant differences between the four samples analyzed. The peak at ~ 60 ppm is due to the framework Al, and it is present in all four samples with roughly equal concentrations. This indicates that no significant dealumination of HZSM-5 occurred during the one hour catalytic upgrading of the aqueous oil fraction at 500 ^{o}C. This result was supported by the NH_3-TPD measurements, which showed that all spent catalysts retained their total acidity after combustion of the coke on the catalysts. Fresh HZSM-5 catalyst had 773 μmol/g total acid sites and the NH_3-TPD measurements of the regenerated catalysts were all within ± 5 % of this amount. Previous studies have reported that steam causes irreversible deactivation of HZSM-5 through dealumination.[11, 53] Dealumination was not observed in our experiments possibly because of the relatively short duration of the runs. There have been some studies, which show that dealumination can be minimized by addition of phosphorous to HZSM-5.[53-54]

3.3. GCMS Results. These experiments were conducted to identify products observed in the MBMS studies above. This experiment used excess catalysts, so the products measured will be similar to those measured at the beginning of the MBMS experiments. Table S2, lists the products observed from upgrading the aqueous oil with fresh excess HZSM-5. Fresh HZSM-5 upgrades the organics in the aqueous fraction to form olefins (ethylene, propylene, 1-Propene, 2-methyl and 1-butene) and aromatic hydrocarbons (benzene and alkylated benzenes, naphthalene and alkylated naphthalenes, anthracene and alkylated anthracenes, indene and alkylated indenes) and oxygen is rejected through H_2O, CO and CO_2. This agrees with products observed in Figure 2 from the MBMS study above and previous studies on catalytic fast pyrolysis of carbohydrates[5, 42, 50-51] and bio-oil aqueous phase[11, 13-14] using HZSM-5. Neither phenols nor naphthols were observed in the py-GCMS study because the concentration of coke precursors was low under the conditions (1 μl aqueous oil and 20 mg HZSM-5) for this experiment.

4. CONCLUSION

This work studied the product distribution formed during catalytic upgrading of the aqueous bio-oil fraction using HZSM-5 catalyst. The significant results from this study can be summarized as follows:

1. Initially, HZSM-5 upgrades the oxygenated species in the oil mostly to small olefins and aromatic hydrocarbons. The yield of these products reached 40 % based on carbon in the feedstock.
2 With time on stream the production of hydrocarbon decreased and that of oxygenated products such as phenols, naphthols, and furans increased. A suite of coke precursors was stripped-off by steam leading to extended catalyst lifetime compared to that observed during processing biomass or the whole bio-oil.
3. The excess water in the feed reduced the amount of coke deposited on HZSM-5 catalyst by either reacting with coke precursors to form other products or by competing with organic species for adsorption sites on the HZSM-5 catalyst surface. It also seemed to cause a steric effect on the reaction intermediates, which impacts the selectivity favoring formation of one-ring aromatic hydrocarbons over polyaromatic hydrocarbons.
4. There was no evidence for HZSM-5 dealumination from both ^{27}Al NMR and NH_3 TPD studies. The catalyst regained their original acidity after regeneration.
5. A high activity catalyst is required for producing aromatic hydrocarbons for fuels.

Therefore, the catalyst should be regenerated after contacting about one-quarter of its mass of feedstock.

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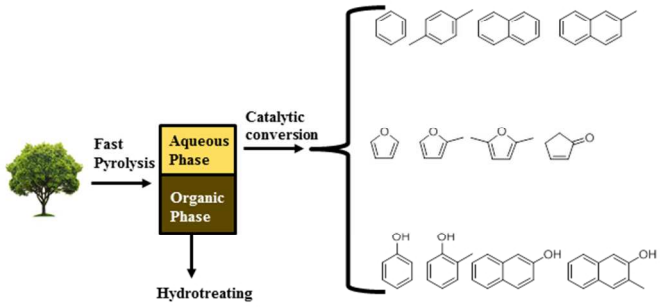
Table 1, Major GCxGC-TOFMS peaks in whole pyrolysis oil and aqueous extraction. Area counts based on extracted ion counts, moisture free basis. The detailed conditions are listed in Table S1(supplementary information).

Compound Name	Whole Oil	Aqueous Phase	% Extracted
Acetic acid	15,668,074	15,755,749	100.56%
2-Propanone, 1-hydroxy-	10,243,435	8,992,486	87.79%
Butanedial	1,274,151	945,720	74.22%
Furfural	2,445,226	801,491	32.78%
2(5H)-Furanone	1,656,412	1,103,011	66.59%
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	432,483	ND[1]	0.00%
Phenol, 2-methoxy-	434,213	ND[1]	0.00%
Phenol, 2-methoxy-4-methyl-	202,076	ND[1]	0.00%
1,2-Benzenediol	790,743	183,429	23.20%
Phenol, 2,6-dimethoxy-	326,691	ND[1]	0.00%
á-D-Glucopyranose, 1,6-anhydro-	27,647,192	12,910,349	46.70%

[1]ND = Not Detected

Table 2. Carbon yields for the H-ZSM-5 conversion of organic available in the bio-oil aqueous phase using py-MBMS. Reaction conditions: Aqueous fraction vapor upgrading at 500 °C, 1 atm, WHSV ~ 1 h^{-1}, 1.0 g catalyst.

	Carbon yield, wt %							
Time interval	CO	CO_2	C_2-C_4	BTX	Furans	Phenols and naphthols	Naphthalenes and anthracenes	Total
10-20	37.5	10.9	9.0	25.0	1.3	4.7	6.0	94.3
20-30	36.2	13.1	11.8	18.4	5.1	6.0	3.7	94.3
30-40	29.8	14.5	17.4	12.1	8.1	5.9	2.2	89.9



This work will enable development of methods for upgrading organics in biomass pyrolysis aqueous phases.

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