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Petroleomic Characterization of Bio-Oil Aging using Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry†

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Bio-oil instability, or aging, is a significant problem for the long-term storage of fast pyrolysis oils. We investigated bio-oil aging at the molecular level using Fourier-transform ion cyclotron resonance mass spectrometry. Petroleomic analysis suggests that bio-oil aging is resulted from the oligomerization of phenolic lignin products whereas 'sugaric' cellulose/hemicellulose products have negligible effect.

Key Words : FTICR, Petroleomics, Bio-oil, Aging, Mass spectrometry

Introduction

An important advantage of fast pyrolysis oils or bio-oils, compared to other renewable energies such as solar or wind energy, is their storability as a liquid fuel; however, storage procedures currently in place for petroleum crude oils cannot be directly applied to bio-oils due to the significant difference in their chemical properties. These differences in chemical properties arise mostly from the high oxygen content of biomass pyrolysis oils.[1] The high oxygen content is also known to make bio-oil very reactive. During prolonged storage, the reactivity causes the bio-oil to form higher molecular-weight compounds, which increases the overall viscosity of the bio-oil.[2] The increase in viscosity and the corresponding decrease in volatility make the use of bio-oils in fuel applications very problematic since these are undesirable characteristics in transportation fuels.[3]

Several approaches for stabilizing bio-oil have been proposed that focus on decreasing the viscosity of the aged bio-oil. One common practice is to preheat the oil before combustion to lower the viscosity.[4] Preheating bio-oil has been shown to accelerate polymerization reactions and to cause phase separation of the bio-oil. As a result, preheating the oil may lead to particulates clogging the fuel lines.[2] Another approach to dealing with the increased viscosity is to dilute the bio-oil with an alcohol. The bio-oil diluted in alcohol is known to slow down the polymerization reactions.[5] Unfortunately, the addition of alcohol to stabilize bio-oil is not economically feasible.

Currently, the most common procedure for studying bio-oil stability was developed by Diebold and Czernik.[5] This procedure involves 'rapidly aging bio-oil' by heating the bio-oil at a mild temperature (usually 90 °C) for a certain amount of time (usually 24 h). Physical measurements, like viscosity and water content, are made before and after the rapid aging procedure. A round robin study of this methodology showed huge variation in the test results.[6] Oasmaa and co-workers claim that the inconsistencies in the round-robin study was probably caused by a lack of experience in the laboratories.[2]

Brown and co-workers have been coupling the traditional physical measurements with gel permeation chromatography (GPC) to further study bio-oil aging.[7] This has allowed for the increases in the molecular weight distribution observed by GPC to be correlated with an increase in viscosity that occurs as the bio-oil ages. Studies have also been conducted that examine the bio-oil aging progression by dividing the 24 h rapid aging test into 8 h increments. They found that most of the aging occurs within the first 8 h increment of the rapid aging test. This first 8 h increment showed a sharp decrease in lower molecular weight compounds (< 100 Da) and an increase in higher molecular weight compounds.[7]

Gel permeation chromatography provides the molecular weight distribution or degree of polymerization of bio-oil aging,[7] but it cannot provide molecular information of the higher molecular weight compounds. A better understanding of the molecular constituents involved in bio-oil aging is expected to provide better insight into how to stabilize the bio-oil and/or slow down the aging process. Gas chromatography-mass spectrometry (GC-MS) has been widely utilized to study bio-oil,[8] but GC-MS is limited to analyzing only volatile and low molecular weight compounds of bio-oil. In addition, it cannot provide molecular information of the compounds not present in NIST EI-MS database. Hence, there is still a need for an analytical tool to examine bio-oil aging at molecular level, specifically for the higher molecular weight compounds. Marshall and coworkers have developed a high-resolution mass spectrometry (HRMS) approach to directly analyze chemical compositions of thousands of compounds in petroleum oils and understand their molecular characteristics, named as petroleomics.[9] Previously, we have reported the successful use of a petroleomics approach to characterize bio-oils at the molecular-level.[10-12] Here we apply this approach to bio-oil aging to understand the associated molecular changes. Electrospray ionization

†This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

(ESI) in negative ion mode and atmospheric pressure photoionization (APPI) in positive ion mode were used for the current study, which are widely used for the petroleum crude oil analysis.[13,14]

Experimental

Fast Pyrolysis and Rapid Aging. The bio-oil samples were provided by the Brown Group at Iowa State University. In short, the bio-oil was produced by fast pyrolysis of red oak with a pilot-scale fluidized bed reactor located at the Biocentury Research Farm at Iowa State University.[8] The samples were then subjected to an accelerated aging procedure by heating at 90 °C for 0, 8, 16, and 24 h (T0, T1, T2, and T3). These increments have been shown to represent 0-12 months of naturally occurring aging of bio-oil at room temperature.[3] The rapid aging samples were diluted in methanol at a concentration of 1 mg mL^{-1} and stored at 4 °C until analysis. Nalgene bottles were used to store the bio-oils because of their chemical resistivity. The bio-oil samples were further diluted right before analysis to a concentration of 0.1 mg mL^{-1} in a solvent mixture that is appropriate for the specific ionization technique being used. The solvent mixture for (−) electrospray ionization (ESI) was 50% methanol in water and the solvent mixture for (+) atmospheric pressure photoionization (APPI) was 15% toluene in methanol.

Mass Spectrometry. The bio-oil samples were analyzed with two Fourier transform ion cyclotron resonance (FTICR) MS: 7T SolariX FTICR MS at Iowa State University for ESI experiments and 12T SolariX FTICR MS at Bruker facility in Billerica, MA, USA, for APPI experiments. ESI was run in negative-ion mode and APPI was operated in positive-ion mode. Each instrument was carefully tuned for the mass range of interest and to minimize possible aggregation and/or fragmentation of the bio-oil compounds.[11]

Data Analysis. The FTICR data was first calibrated with DataAnalysis software (Bruker) using known bio-oil peaks. The calibrated data was then imported to Composer (Sierra Analytics, Modesto, CA, USA) where it was further calibrated using a homologous series algorithm and assigned chemical compositions based on accurate mass. The mass accuracy of the assigned chemical compositions was limited to less than 3 ppm, and the relative abundance threshold for peaks being included in the analysis was 0.1%.

Results and Discussion

(+) Atmospheric Pressure Photoionization. The APPI-FTICR MS spectra were acquired in positive ion mode for three bio-oil aging samples (T1, T2, and T3) and a control (T0), and T0 and T3 spectra are compared in Figure 1. The *m/z* ranges observed in the two spectra are from *m/z* 150 to 900. Overall peak patterns are similar between the two with an average molecular mass slightly higher in T3. With a closer look, the high mass tail is much more prevalent in the T3 spectrum. For example, the peaks at *m/z* range of 500-580 in T3 has an equivalent relative abundance of that at *m/z* range of 430-500 in T0.

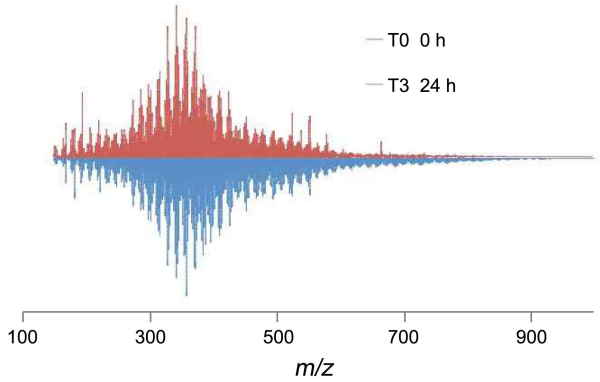

Figure 1. The (+) APPI mass spectra for un-aged bio-oil (T0, top red) and bio-oil that has been aged at 90 °C for 24 h (T3, bottom blue).

Chemical composition analysis was performed for all four FTICR MS datasets. Both radical and protonated ions are produced by (+) APPI; however, there was no significant difference between radical and protonated ions in bio-oil samples in terms of overall heteroatom class distributions. Hence, the rest of the analysis was focused on protonated species because of their higher relative abundance in the presence of toluene dopant. The heteroatom class distributions for the four bio-oil aging samples are shown in Figure 2. The (+) APPI FTICR data of red oak bio-oil show only oxygen containing compounds, with the number of oxygen ranging from 0 (HC; hydrogen and carbon only) to 15. Compared to the bio-oil sample that did not undergo aging (T0), the ion abundance of aged samples (T1-T3) decreases in low oxygen compounds (O2-06) and increases in high oxygen compounds (O8 and higher) as the aging progress. This is in good correlation with Figure 1 in the fact that high mass compounds have higher oxygen content.

Double bond equivalence (DBE; the number of double bonds plus cyclic ring) is calculated from the following equation DBE = x − ½y + ½z + 1, with x, y and z being the number of carbon, hydrogen and nitrogen atoms, respectively. This is another useful tool in understanding complex bio-oil samples. APPI is well known to preferentially ionize aromatic compounds.[14] In case of bio-oils, phenolic compounds

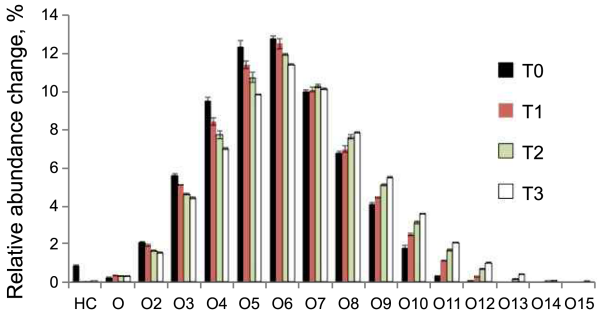

Figure 2. The protonated heteroatom class distribution of bio-oil aging samples obtained in (+) APPI-FTICR MS.

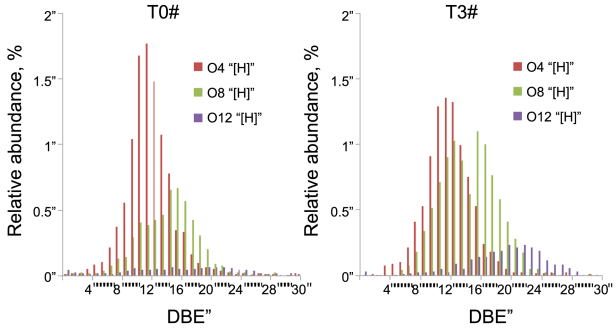

Figure 3. DBE distribution of T0 and T3 bio-oil aging samples for O4, O8, and O12 heteroatom classes in (+) APPI.

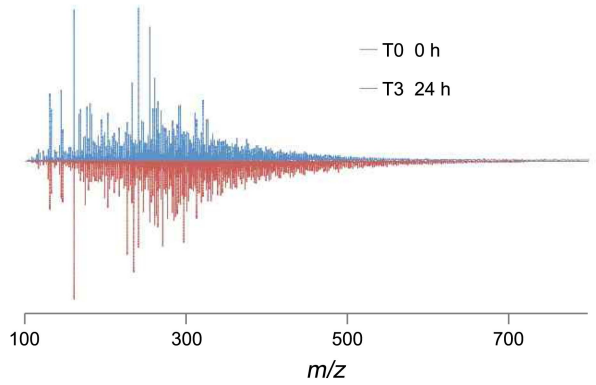

Figure 4. (–) ESI mass spectra for un-aged bio-oil (T0, top red) and after aging at 90 °C for 24 h (T3, bottom blue).

produced from lignin pyrolysis are the major compounds ionized by APPI. Each lignin monomeric unit has a minimum DBE value of four (*i.e.* benzene ring) and average DBE of about five (including one carbonyl or vinyl side chain).[10] Hence, we can estimate the degree of oligomerization in lignin pyrolysis products by dividing their DBE values by 5.

The DBE distribution of a few major heteroatom classes is shown in Figure 3 for T0 and T3 bio-oils. The overall distribution is similar for O4 class between T0 and T3 samples, specifically most abundant at DBE of 12 (dimer or trimer) and widely distributed over the range of 5-20 (monomer to tetramer); however, the relative abundance of the O4 class is decreased by 20-25% for T3 compared to T0. The O12 class is present in almost negligible amount for T0 but significant in T3 and most abundant at DBE of 20-23 (tetramer or pentamer). The O8 class compound is quite interesting for having two distinct distributions, one peak at DBE of ~12 and the other at ~16. The O8 relative abundance is increased by two-fold with T3 compared to T0. This data clearly suggests that the decrease of smaller oligomers (dimer or trimer) and the increase of bigger oligomers (tetramer or higher) as bio-oil aging.

(–) Electrospray Ionization. To examine the effects of polar compounds on bio-oil aging, the bio-oil aging samples were analyzed using negative-mode electrospray ionization. (–) ESI has been previously shown to readily ionize both aliphatic (or sugar) and aromatic (or phenolic) compounds of bio-oil as deprotonated ions, $[M\text{-}H]^-$.[11] The spectra obtained for T0 (blue, top) and T3 (red, bottom) samples, in Figure 4, show only a slight increase of high mass compounds.

As we have previously reported,[11] we can observe both cellulose/hemicellulose pyrolysis products and lignin pyrolysis products in (–) ESI. They can be easily distinguished from the difference in their DBE values. We separated the two heteroatom class distributions as shown in Figure 5. Here we define "sugaric" compounds as those with DBEs of three or less and "phenolic" compounds as those with DBE of four or higher. "Sugaric" compounds are cellulose and hemicellulose derived pyrolysis products like levoglucosan and "phenolic" compounds are from lignin pyrolysis.[11] Furans like hydroxymethyl furfural are five-membered aromatic compounds with a DBE of 3 and indistinguishable from some compounds like levoglucosenone (DBE of 3). In any case, they could still be counted as "sugaric" compounds because they are pyrolysis products of hemicellulose and cellulose. It should be noted this classification has some limitations as some of them might be overlapping. For example, furan or levoglucosenone with an additional double bond (from carbonyl or alkenyl side chain) will have a DBE value of 4 and counted as "phenolic". However, such contribution is expected to be minimal.

The heteroatom class distribution for "sugaric" compounds (Figure 5, top) is similar between the two bio-oil aged samples. The slight difference in relative abundance for O5 and O8 compounds is attributed to pH matrix effects. We have previously reported that the relative abundance of levoglucosan (anhydrous glucose, $C_6H_{10}O_5$, O5 with DBE of 2; *m/z* 161, the highest abundance peak in Figure 4) is subject to pH matrix effects and shows the decrease of ion abundance at low pH.[11] It should be noted there is no apparent difference for the *m/z* 161 peak in Figure 4 because the spectra are normalized to the highest abundance peak (*m/z* 161), but the relative ion abundance of *m/z* 161 is ~25% less for T3 when the spectra are normalized to the total ion

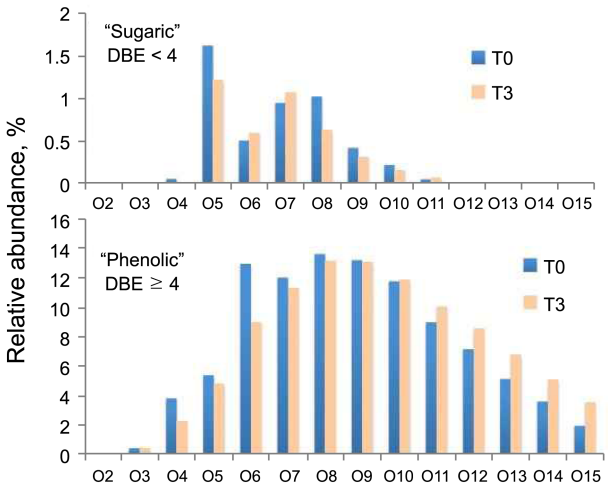

Figure 5. Heteroatom class distributions for "sugaric" (DBE < 4) and "phenolic" (DBE 4) compounds for T0 and T3 samples.

count.

The aging effect is more apparent in the heteroatom class distribution of aromatic compounds (Figure 5, bottom) and shows a similar trend with (+) APPI data: a decrease of lower oxygen compounds and increase of higher oxygen compounds. This suggests that bio-oil aging mostly arises from the oligomerization of lignin pyrolysis products. Several possible aging mechanisms have been proposed including oxidation-induced reactions and esterifications.[4] Among those, acid catalyzed reactions of phenolic compounds is a possible mechanism for the oligomerization of lignin products.

Phenolic compounds observed in (−) ESI and (+) APPI have slightly different chemical functionalities. Phenolic compounds in (−) ESI have on average two or three more oxygens than in (+) APPI with the most abundant heteroatom class of O8/O9. This distribution extends beyond O15 (O16 and higher heteroatom classes are not shown) whereas in (+) APPI most abundant heteroatom class is O6 and very minimal for heteroatom classes above O14. This difference arises from their difference in ionization efficiencies; (−) ESI preferentially ionizes compounds that can be readily deprotonated whereas (+) APPI preferentially ionizes compounds that can be readily protonated. While most phenolic compounds can be ionized by both modes, some compounds show a much higher abundance in one mode versus another. For example, phenolic compounds with a carboxylic group, *e.g.* vanillic acid, have a much higher abundance in (−) ESI. The fact that both (+) APPI and (−) ESI support the oligomerization of phenolic compounds in spite of the difference in ionization preference indicates that bio-oil aging occurs in a wide class of lignin pyrolysis products.

Conclusion

We have performed a petroleomic analysis of bio-oil aging utilizing high-resolution FTICR. We conclude that the problems with bio-oil stability arise mostly from the oligomerization of lignin derived pyrolysis products. This is supported by both (+) APPI and (−) ESI data for a wide class of lignin pyrolysis products. In contrast, "sugaric" compounds in (−) ESI (DBE < 4), specifically cellulose and hemicellulose pyrolysis products, show almost a negligible effect by aging.

It should be noted there are several limitations in the current analysis. Petroleomic analysis are not amenable to characterize low mass compounds (*i.e.* MW < 100) whereas the change in pH should mostly arise from low oxygenates such as formic and acetic acids. We have observed dramatic change of a few ion peaks in (−) ESI with aging (Figure 4); however, we did not pursue detailed analysis of their origin because it is partially due to the pH matrix effect and is difficult to calibrate for without the exact knowledge of their identities. Nevertheless, our study demonstrated the molecular weight increase in bio-oil aging is most likely due to the oligomerization of phenolic compounds from lignin pyrolysis.

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