Separation of Switchgrass Bio-oil by Water/Organic Solvent Addition and pH Adjustment

Lydia Kyoung-Eun Park,[†] *Shoujie Ren,*[‡] *Sotira Yiacoumi,*[†] *X. Philip Ye,*[‡] *Abhijeet P. Borole,*[‖,⊥] *and Costas Tsouris*[†,⊥,*]

† Georgia Institute of Technology, Atlanta, Georgia 30332-0373, United States

‡ The University of Tennessee, Institute of Agriculture, Knoxville Tennessee 37996-4514, United States

‖ Bredesen Center for Interdisciplinary Research and Education, The University of Tennessee, Knoxville, Tennessee 37996-4514, United States

⊥ Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6181, United States

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ABSTRACT

Applications of bio-oil are limited by its challenging properties including high moisture content, low pH, high viscosity, high oxygen content, and low heating value. Separation of switchgrass bio-oil components by adding water, organic solvents (hexadecane and octane), and sodium

hydroxide may help to overcome these issues. Acetic acid and phenolic compounds were extracted in aqueous and organic phases, respectively. Polar chemicals, such as acetic acid, did not partition in the organic solvent phase. Acetic acid in the aqueous phase after extraction is beneficial for a microbial-electrolysis-cell application to produce hydrogen as an energy source for further hydrodeoxygenation of bio-oil. Organic solvents extracted more chemicals from bio-oil in combined than in sequential extraction; however, organic solvents partitioned into the aqueous phase in combined extraction. When sodium hydroxide was added to adjust the pH of aqueous bio-oil, organic-phase precipitation occurred. As the pH was increased, a biphasic aqueous/organic dispersion was formed, and phase separation was optimized at approximately pH 6. The neutralized organic bio-oil had approximately 37 % less oxygen and 100 % increased heating value than the initial centrifuged bio-oil. The less oxygen content and increased heating value indicated a significant improvement of the bio-oil quality through neutralization.

1. INTRODUCTION

The U.S. Energy Information Administration forecasts that by 2040 the world energy consumption will increase 56 %.[1] While the energy consumption is expected to increase, use of fossil fuels, currently the main energy source, is expected to decrease because of their suspected contribution to global warming. One of the candidates to substitute fossil fuels is biofuels utilizing biomass.[2] There is enough biomass from available land resources to accomplish the goal of replacing 30 % of fossil fuels with biofuels by 2030 according to a joint report by the U.S. Departments of Agriculture and Energy.[3] Biomass products are currently used as fuel additives such as biodiesel and ethanol.

Another type of biofuel, bio-oil or pyrolysis oil is a liquid condensate of vapors from biomass pyrolysis, a process of heating biomass in oxygen-limited conditions. Some products of pyrolysis

include char, syngas, bio-oil, CO_2 and C_1-C_4 hydrocarbons (e.g. CH_4, C_2H_6, C_3H_8, C_4H_{10}). Depending on the biomass materials, reactor designs, and reaction conditions including heating rates and reaction temperature, the chemical and physical properties of bio-oil can vary. Although bio-oil has a significant potential as an energy source, challenging properties of bio-oil such as non-homogeneity, high moisture content, high viscosity, high density, high oxygen content and high acidity can limit its applications. High acidity is especially problematic in transportation and storage of bio-oil. Moreover, due to high moisture content, bio-oil has a low calorific value. Thus, bio-oil needs to be upgraded before it can be efficiently used as an energy source.

Many research groups have previously investigated various approaches to improving bio-oil quality. Some proposed upgrading technologies are hydrodeoxygenation,[4] supercritical fluid extraction,[5] reactive distillation,[6, 7] catalysis,[4] esterification,[8] and water addition.[9-11] Among various physical and chemical upgrading treatments of bio-oil, phase separation has been critical for further processing of bio-oil. The addition of water to bio-oil is known to form two phases,[9-11] and has been commonly used to separate water-soluble components or aqueous phase on top. Song et al.[12] examined the effect of aqueous salt solutions or solid salts on phase separation of bio-oil. Previous research on the solvent extraction of bio-oil using cyclohexane, dichloromethane, ethyl acetate, and butyl acetate demonstrated that dichloromethane was the most effective solvent for extracting chemicals, especially alcohols and acids from bio-oil.[13] Recently, liquid-liquid extraction of bio-oil was investigated using several solvents including hexane, petroleum ether, and chloroform.[14] Among these three solvents, chloroform was the most effective in extracting phenols and guaiacols.[14] With chloroform added to aqueous phase bio-oil (i.e., water phase separated after adding water to bio-oil at 1:1 volume ratio) at a volume

ratio of 1:1, chloroform extracted 85.7 wt% of the total phenols and guaiacol in the water-phase.[14, 15] Furthermore, Ma et al. separated fractions of bio-oil by sequentially contacting with hexane, toluene, chloroform, and methanol in the order of increasing polarity.[15] It was found that as the polarity of extraction solvent increased, the viscosity of fractions increased.[15] Consequently, liquid extraction has the potential to extract some valuable chemicals and improve the bio-oil quality.

In addition to phase separation, separating organic acids (e.g., acetic acid) that cause high acidity and corrosivity of bio-oil is important in upgrading bio-oil. Reactive extraction using long-chain tertiary amines,[16] nanofiltration, and reverse osmosis membrane[17] recovered acetic acid from bio-oil. The extracted organic acids can be utilized to produce another valuable energy source, hydrogen. Hydrogen is also required to upgrade bio-oil via hydrodeoxygenation. Today, hydrogen in hydrodeoxygenation is commonly supplied by natural gas.[18] To find a replacement of natural gas, Lewis et al.[19] recently demonstrated hydrogen production via microbial electrolysis cell (MEC) using the aqueous phase of bio-oil, which contains organic acids. By separating organic acids, the acidity and corrosivity problem of bio-oil would be resolved.

Here, for separating organic acids, liquid-liquid extraction using water and/or organic solvents is investigated. Different extraction methods, such as combined and sequential aqueous/organic extractions, are compared. For combined extraction, both water and organic solvents are contacted with the aqueous bio-oil (AqBO) – centrifuged bio-oil – at the same time. In sequential extraction, water is added first with the AqBO. Then, the separated organic phase is contacted with organic solvent sequentially. The motivation behind extraction experiments using organic solvents, octane and hexadecane, is to utilize some chemical components in the bio-oil as fuel additives. Octane and hexadecane were used as model molecules representative of gasoline and

diesel, respectively. Although liquid extraction may not efficiently separate chemicals from bio-oil, it can selectively separate certain groups of chemicals from bio-oil.

Along with many other organic compounds present in the bio-oil, phenolics contribute to high oxygen content. The oxygen content can be lowered, and the stability of bio-oil can be increased by removing phenolics from bio-oil. Phenolics, usually produced from fossil fuels, are valuable chemicals in producing phenolic resins, fine chemicals, pharmaceuticals, and food processing.[20] Approaches to producing phenolic resins from bio-oil are described in a review article.[21] Currently, chemical conversion through hydrodeoxygenation and physical removal through extraction are the two main ways to lower the content of phenolics in bio-oil. Hydrodeoxygenation of phenol to cycloalkane using metal catalysts in the presence of acids can overcome the phenolics-associated problems.[22] Alternatively, Guo et al.[23] converted phenolic compounds into alcohols using Ru/SBA-15 catalyst. Furthermore, Zilnik and Jazbinšek[24] extracted phenolics by adding sodium hydroxide (NaOH) solution, followed by butyl acetate. Wang et al.[25] changed the pH by using NaOH and hydrochloric acid in multiple steps to extract neutral and phenolic fractions from an organic phase. In this study, instead of using the organic phase, we used AqBO to further remove phenolics so the precipitated organic phase (NBoop: for neutralized bio-oil phase) may be treated further to produce phenolic resins, fuel additives, or replacement of fossil fuels. To find optimal conditions for phenolic separation from the AqBO, the AqBO was adjusted to various pH values using NaOH.

The objectives of this research are to find optimal conditions for phase separation of bio-oil: an aqueous bio-oil phase for producing hydrogen by microbial electrolysis and an organic phase for obtaining valuable chemicals and fuel additives. Phase separation is crucial for separating acids from the bio-oil to lower its acidity, and for removing phenolics from the aqueous phase to lower

the oxygen content and produce valuable chemicals. Due to the heterogeneity of bio-oil, all the experiments use the AqBO after centrifuging crude bio-oil produced from intermediate pyrolysis of switchgrass via an auger reactor.

2. EXPERIMENTAL SECTION

2.1 Production of Bio-oil

Switchgrass intermediate pyrolysis for bio-oil production was conducted with a semi pilot-scaled auger pyrolysis system (Proton Power, Inc., Lenoir City, TN, USA) at the Center for Renewable Carbon of The University of Tennessee (UT). The auger pyrolysis system was composed of a feeding system with hopper and single auger, a rectangular auger reactor (10 W×10 H×250 L cm) with dual augers, a pyrolysis vapor condensation section, a particle precipitating chamber, and a biochar collector (Figure S1). Air-dried switchgrass (Panicum virgatum L.) obtained from a local producer in eastern Tennessee was used as biomass feedstock for bio-oil production. The details of switchgrass compositions were described in a previous report.[26] Briefly, the contents of cellulose, hemicellulose, and lignin were approximately 34 %, 26 %, and 19 %, respectively, based on dry biomass. Before pyrolysis, switchgrass was ground to less than 2-mm particle size. Switchgrass pyrolysis was conducted at 500 °C with a residence time of 90 s and feeding rate of 10 kg h^{-1} in the presence of N_2. In this study, a mass of 20 kg switchgrass was pyrolyzed for bio-oil production. The water content of switchgrass was about 7-8 wt. %.

2.2 Physical Properties of Bio-oil

Physical properties such as density, pH range, viscosity, water content, solid content, ash content, total acid number (TAN), oxygen content, and heating value were first determined for

bio-oil (Table 1). Each measurement was conducted in triplicate. The bio-oil density was measured according to the standard ASTM D1217 method with a pycnometer.[27] The pH was measured with an Extech pH meter. The water content was measured with a Schott TitroLine Karl Fischer volumetric titrator according to the ASTM D4377 standard.[28] The viscosity was measured at 40 °C with serialized Schott Ubbelohde capillary viscometers according to the ASTM D445 standard.[29] The ash content was measured according to the ASTM D482 standard at 575 °C.[30] The methanol-insoluble materials in bio-oil were measured to determine the solid content according to Boucher et al.[31] The TAN was measured by titrating bio-oil in the solvent of isopropyl alcohol and toluene with 0.1M KOH isopropyl alcohol solution to an endpoint of pH 11 according to the ASTM D664 standard.[32] The oxygen content and heating value were analyzed by ALS Environmental (Tucson, Arizona) following the ASTM D5373 M - Pyrolysis / IR detection method and ASTM D4809 method, respectively.

2.3 Liquid-Liquid Extraction

Deionized water was used for preparing all aqueous solutions used in the experiments of this study. Hexadecane (C16) and octane (C8) obtained from Sigma-Aldrich were used as representative species for diesel and gasoline, respectively. Crude bio-oil obtained from UT was centrifuged to obtain aqueous bio-oil (AqBO) and organic bio-oil (OrgBO). The nomenclature of bio-oil and phases is summarized in Abbreviation. The AqBO refers to the supernatant after centrifuging crude bio-oil. The OrgBO refers to the precipitate or particles collected at the bottom after centrifugation. After centrifugation of crude bio-oil, the AqBO was 82 wt%, and the OrgBO was 18 wt%. Only the AqBO was used in the experiments described here. In general, the mixture of AqBO and solvents was put in a centrifuge tube and placed in a shaker overnight to reach equilibrium. After reaching equilibrium, the mixture was centrifuged at 3000 rpm for 30

minutes for phase separation. The different phases were separated to measure the weight using a balance (Ohaus Analytical plus).

Combined Extraction

As shown in Scheme 1, the AqBO was mixed with deionized water and C16 or C8 at an arbitrary ratio of 1:2:2 by weight. For phase separation, the mixture was centrifuged after shaking for several hours overnight. The separated phases were analyzed individually using gas chromatography / mass spectrometry (GC-MS). Solvent phases were analyzed without any treatment while the aqueous and bio-oil phases were diluted twenty times with methanol prior to GC-MS analysis.

Sequential Extraction

Deionized water was added to the AqBO at 1:2 weight ratio of AqBO to water. The mixture was shaken overnight. On the next day, the phases were separated after centrifugation. Then, C16 or C8, at the same weight as the initial water, was added to the separated Boop (see Scheme 1) for further extraction. After reaching equilibrium overnight, the different phases were separated after centrifugation for further analysis. Sequential extraction is also summarized in Scheme 1.

2.4 pH Adjustment of Bio-oil

The pH of the AqBO that was obtained from centrifuging crude bio-oil was adjusted by adding NaOH (50%) solution purchased from Sigma-Aldrich. Due to exothermic reactions, when NaOH solution was added to the AqBO (10 g), the temperature of the mixture increased up to 70 ºC. The mixture was centrifuged after it was cooled down to make sure it reached equilibrium, and samples were taken for GC-MS analysis. The pH of the Boap (see Scheme 1) was also measured after centrifugation.

2.5 GC-MS Analysis

GC-MS was performed at the BioAnalytical Mass Spectrometry Facility at the Georgia Institute of Technology (GIT). The column was an Agilent DB-5, 30-m long by 0.25-mm i.d. with a coating thickness of 0.25 μm. The program started with the oven at 35 °C for 1 minute. The oven temperature was ramped to 300 °C at a heating rate of 15 °C/min. Then, the temperature was held at 300 °C for 6.3 minutes. The carrier gas was helium. A sample volume of 1 μL was injected with 50:1 ratio split mode. The inlet temperature was 280 °C. The chemical species were identified from comparing with the mass spectral data library of the National Institute of Standards and Technology. Samples were prepared by diluting twenty times with methanol. The SolvB was analyzed without further treatment.

2.6 High-Performance Liquid Chromatography (HPLC) Analysis

The high-performance liquid chromatography (HPLC) system used was Agilent 1100. A BioRad Aminex HPX-87H column and a refractive index (RI) detector were used in HPLC analysis. The mobile phase was 5 mM sulfuric acid (H_2SO_4), and the flow rate of the mobile phase was 0.6 mL/min. The samples were diluted twenty times with the mobile phase (H_2SO_4). A volume of 20 μL sample was injected, and each sample was run for an hour.

3. RESULTS AND DISCUSSION

3.1 Water Addition

Through centrifugation, the crude bio-oil was separated into water-like aqueous bio-oil (AqBO) and paste-like organic bio-oil (OrgBO). Previous work by other groups showed that phase separation occurred when water was added to bio-oil.[9-11] The centrifuged bio-oil of aqueous bio-oil (AqBO) had oxygen content of 52.77 wt% and heating value of 4,944 BTU/lb.

Deionized water was added to the AqBO at a weight ratio of 1:2 or 1:4 (AqBO to water ratio), as described in Table S1. When water was added to single-phase AqBO, a second paste-like phase, Boop, formed at a relatively small quantity (see Scheme 1 and Table S1). The mass balance and water-content results before and after water addition (1:4 wt.) are presented in Scheme 2. Boap, the aqueous phase obtained from water addition to AqBO was analyzed by GC-MS as shown in Figure S2 (A). The chemicals corresponding to the peak numbers found in GC-MS figures (Figures S2 – S4 and 1 – 2) are summarized in Table S2.

The major peaks found in Boap were hydrophilic chemical species, such as acetic acid (peak #3), 1-hydroxy-2-propanone (#8), and D-allose (#78); while phenolic species with a retention time from 6 to 13 minutes were found as major species in Boop. The acetic acid concentration was calculated from GC-MS spectra using a standard curve. The concentrations of acetic acid in Boap and Boop after water addition to AqBO are presented in Table 2. The concentration of acetic acid was approximately 28 times higher in Boap than in Boop (see Figure S2 and Table 2). Chemical species found in GC-MS analysis were categorized into groups. The relative percent areas of each chemical group were calculated as shown in Table 2. Acid and alcohol groups were found largely in Boap, while phenolics were the major group in the Boop. Boop did not contain 1-hydroxy-2-propanone and D-allose unlike Boap. Most phenolic species were found within a retention time between 7 and 13 minutes. As compared to AqBO, some chemicals [e.g., 2-methyl phenol (#47) and 2,4,-dimethyl phenol (#50)] were not detected in the Boap. These phenolic species were partitioned in the Boop precipitated when water was added. Sugars such as glucopyranose (#53 and 82) and D-allose (#78) were only found in AqBO and Boap. The 1:2 ratio of AqBO to water represents the first step of sequential extraction.

The Boap with organic acids would produce hydrogen via MEC. Lewis et al.[19] produced hydrogen using Boap obtained after adding water to crude bio-oil instead of AqBO. Moreover, it was observed that organic acids, including acetic acid, were transformed under batch and continuous conditions.[19] Although Lewis et al.[19] showed that phenolics were not problematic for MEC, the presence of less phenolic compounds but more organic acids (e.g., acetic acid) in Boap would be preferred for MEC applications. Furthermore, phenolics could be used for the production of higher value chemicals (e.g., phenolic resins).

3.2 Organic Solvent Addition: Hexadecane vs Octane

For organic solvent extraction, hexadecane (C16) and octane (C8) were chosen to represent diesel and gasoline components, respectively. The AqBO was extracted using organic solvents (C16 or C8) with a weight ratio of 1:4 (AqBO to organic solvents) to compare the results of combined and sequential extraction in further analysis.

The AqBO and organic solvents were not miscible; they formed two distinctive phases. The mixtures of AqBO and organic solvents were placed in a shaker overnight to reach equilibrium. The color of both organic solvents changed from colorless to yellow, indicating that some bio-oil components were extracted. The mixtures were separated into different containers after centrifugation by pouring out the solvent phase into a separate container. The changes in the weight of each phase were insignificant. However, the actual amount of AqBO components that partitioned to organic solvent phases (SolvB) might be larger than the overall difference because organic solvents were also partitioned to bio-oil phases (SBoap) as found in Figures S3 (B) and (D).

The SBoap and the SolvB phases after extraction were analyzed by GC-MS as shown in Figure S3. For GC-MS analysis, the SBoap was diluted twenty times with methanol, while organic

solvents were not further treated. It is noteworthy that C16 is a poor solvent for GC-MS analysis. The gas chromatography peaks from 11 to 13.4 minutes in Figure S3 (A) came mostly from C16 and its impurities. It was difficult to distinguish whether some of the chemicals that had similar retention time as C16 were extracted because C16 had a large and wide peak.

The amounts of acetic acid in SolvB and SBoap after organic solvent extraction of AqBO are shown in Table 2. In C16 and C8 phases, acetic acid was not found or was under the detection limit (Table 2). Moreover, the relative percent areas of chemical species groups are shown in Table 2. More than 97 % of chemical species were alkanes. The alkane group was primarily from organic solvents. About 3 % relative percent area came from extracted chemicals. To compare the chemical species extracted, the relative percent areas were calculated by excluding the alkane group (bottom values in Table 2). Organic solvents could extract furan, ketone, and phenolics from AqBO. Phenolic compounds were extracted more by octane (70.6 %) as compared to C16 (34.3 %) according to Table 2. Alcohol was extracted to the hexadecane phase, while aldehyde was extracted to the octane phase. The SBoap was still similar to the initial AqBO. There were no SBoop formed by adding organic solvents, unlike the water addition experiment. The oxygen content and heating value of C8 phase from organic solvent extraction were 1.74 wt% and 20,140 BTU/lb, respectively, and those of C16 were 1.29 wt% and 20,200 BTU/lb, respectively.

3.3 Combined Extraction vs. Sequential Extraction

To determine whether single- or multi-stage extraction in series would be needed in a solvent extraction application, combined and sequential extractions were compared in a small scale. In combined extraction, water and the organic solvent were simultaneously added to bio-oil. Instead, AqBO was initially contacted with water and the resulting Boop was subsequently

contacted with the organic solvent in sequential extraction (see Scheme 1). The reason that water addition was performed first was to prevent organic solvent partitioning into the water phase.

Combined extraction using AqBO formed three different phases: solvent (SolvB), water (SBoap), and organic bio-oil (SBoop) phases. Formation of three phases indicated that even if combined extraction was performed, phase separation would be needed twice. Boap that was less viscous than SBoop became a brown-color liquid containing water-soluble chemicals such as acetic acid (#3), 1-hydroxy-2-propanone (#8), and D-allose (#78). The SolvB was organic solvent with extracted chemicals such as phenolics. The SBoop was dark-brown, paste-like liquid that was similar to the Boop formed after water addition. The amounts of phases from combined and sequential extraction are presented in Table 3. Moreover, the mass balances with water content results are presented in Scheme 3 for combined extraction with C8 and in Scheme 4 for sequential extraction with C8. The changes in the weight of SolvB were insignificant indicating that no significant amounts of chemicals were extracted. However, the actual amount of chemicals extracted would be more than the weight changes indicated because organic solvents also partitioned to other phases. As found in Figures S4 and 1 and Table 2, the acetic acid in SolvB was under the detection limit. There was more acetic acid in the SBoap than in SBoop (Table 2). Phenolics were present the least in the water phases (Table 2). Methanol, the solvent used for the analysis of water and bio-oil samples, was not included in the relative percent area calculation. The SolvB-C16 from combined extraction included alcohols (20.2%), aldehydes (0.5 %), furans (12.8 %), ketones (7.5 %), and phenolics (59 %) while the SolvB-C8 from combined extraction included ketones (7.4 %) and phenolics (92.6 %) excluding alkanes (Table 2). As found in zoomed-in graphs in the upper right-hand corner of Figures S4 (A) and 1

(A), phenolic species extracted by C16 and C8 were similar. C16 extracted a variety of chemicals as compared to C8 (Table 2).

The first step of sequential extraction was similar to the water addition experiment discussed previously, with a 1:2 AqBO to water ratio. Because the organic solvent was added to the system in the second step, the Boap from sequential extraction did not contain organic solvent unlike the SBoap from combined extraction. The Boop formed after water addition was contacted with organic solvents as the second step. Thus, the amount of chemicals exposed to organic solvents was smaller than those from combined extraction. The SolvB from sequential extraction was analyzed by GC-MS (Figure 2). Phenolics were found in SolvB at retention times from 6 to 13 minutes (mostly from 7 to 11 minutes). Some phenolic compounds were present in all SolvB including 4-ethyl-phenol (#51), 2-methoxy-4-methyl-phenol (#52), and 4-ethyl-2-methoxy-phenol (#60) (Figures 1 – 2 and S4). From Table 2, the majority of chemicals in the SolvB detected by GC-MS are alkanes, which originated from organic solvents. This result indicated that about 1 % of relative percent area came from extracted chemicals. According to Table 2 (bottom values), without alkanes, the majority of chemicals extracted by octane were phenolics. More diverse chemical species were found in the SolvB-C16 as compared to the SolvB-C8. As in the combined extraction, the phenolic species found in the SolvB-C16 and SolvB-C8 phases were similar, as shown in the close-up view of Figures 2 (A) and (C).

As shown in Table 3, the changes in the amounts of each phase from combined extraction and sequential extraction were comparable in general. However, according to GC-MS analysis, a larger variety of chemicals were found in SolvB from combined extraction than from sequential extraction (Table 2). The relative percent areas of phenolic compounds in SolvB from combined extraction were higher than those from sequential extraction (Table 2). Therefore, combined

extraction was considered better for extracting more phenolics by organic solvents. On the other hand, sequential extraction would be preferred for extracting more acetic acid by water without organic solvent partitioning to the water phase. Initially, combined and sequential extractions were compared to determine the number of extraction stages needed. One extraction stage for combined extraction and two for sequential extraction were assumed. However, even with combined extraction, two separation steps would be needed because three different phases formed. For extracting more chemicals both in quantity and variety, the combined extraction method would be preferred over the sequential extraction method. In contrast, the sequential extraction would be beneficial for further application of Boap in microbial electrolysis cells because having no organic solvents partitioned to the water phase would minimize the loss of the solvent.

3.4 pH Adjustment of Aqueous Bio-oil

The pH of AqBO was adjusted by adding NaOH (50%) solution. The motivation behind these experiments was that pH neutralization generally increases the concentration of non-ionized species with lower solubility in the solution. Thus, an increase in pH was expected to reduce the solubility of organic species in the AqBO and to form an easily separable insoluble organic phase. This general trend, however, would not apply to some species, such as acetic acid. The pH value of crude bio-oil is between 2 and 3. The pKa value for acetic acid is 4.76. Therefore, most acetic acid would be present as the non-ionized form (CH_3COOH) in bio-oil at low pH, and as the ionized or deprotonated form (CH_3COO^-) at high pH. By adding 50% NaOH solution to AqBO, the pH value increased. The Boop, which contained chemicals including phenolics, precipitated as the pH increased. Scheme 5 shows the mass balance and water content results before and after pH adjustment (pH 6). Figure 3 presents the conductivity of NBoap as a function

of pH. The conductivity of Boap increased as the pH value increased from 3 to 6.3. This increase in the conductivity indicated that the concentration of charged species, e.g., acetate, increased in the Boap. In basic Boap, the conductivity did not increase much as more NaOH solution was added. This plateau showed that most of deprotonation or speciation changes occur at low pH. Visual inspection revealed that the viscosity of the precipitated Boop also increased as the pH values increased. The optimum pH value with respect to percent weight of precipitated Boop seems to be around 6. The oxygen content and heating value of neutralized organic bio-oil (NBoop) around pH 6 were 33.10 wt% and 9,878 BTU/lb, respectively. These data reveal that the oxygen content of neutralized bio-oil decreased by 37 % and the heating value increased by 100 % compared to the centrifuged bio-oil that was used for neutralization.

The amount of total acetic acid and acetate present in the Boap of pH-adjusted bio-oil was measured by HPLC analysis as shown in Figure 4. After dilution with the mobile phase (H_2SO_4), the pH of Boap samples became close to that of sulfuric acid (pH ~2). At around pH 2, acetate would become protonated and exist mostly as acetic acid, which was detected by HPLC. Thus, the measured acetic acid concentration would be roughly the same as the total concentration of acetate and acetic acid. The concentrations of acetate and acetic acid species were calculated using a pKa value of 4.76 and the measured acetic acid concentration at around pH 9 as total acetic acid concentration are found in Figure 4. Changes in the pH value of Boap as a function of 50 % NaOH solution added to 10 g of AqBO are plotted in Figure 4. The Boop formed by addition of NaOH contained mostly phenolic compounds as shown in the chromatogram in Figure 5 (A). Various phenolic compounds were found in the Boop, according to GC-MS analysis unlike the aqueous phase in Figure 5 (B) that contained mainly hydrophilic species such as acetic acid, 1-hydroxy-2-propanone, and D-allose. The remaining NBoap after precipitation of

the NBoop will be investigated in future work for its suitability as feedstock for a microbial electrolysis process to produce hydrogen.

4. CONCLUSIONS

Bio-oil phases are separated by adding water, organic solvents, and NaOH solution. The organic solvent phases contain phenolics and acetic acid. The mass of chemicals extracted by organic solvents is relatively small. Combined extraction is preferred for extracting more chemicals, especially phenolics. Sequential extraction is beneficial for a microbial electrolysis cell application for hydrogen production because organic solvents do not partition into the water phase. When the pH of the AqBO increases, an organic phase with phenolics is formed. The formation of organic phases is optimized at around pH 6. An application of the phenolics stream is needed for the improvement of process economics. The NBoap with hydrophilic chemicals will be further investigated as a feedstock for MEC to produce hydrogen. Furthermore, NBoop contained 37 % less oxygen and had double heating value compared to AqBO, which was used for neutralization. Less oxygen content and increased heating value of NBoop demonstrate a significant quality improvement introduced by bio-oil neutralization.

ABBREVIATION

AqBO: Aqueous bio-oil; water-like, less viscous supernatant liquid obtained from centrifuging crude bio-oil

OrgBO: Organic bio-oil; paste-like, more viscous precipitate or pellet obtained from centrifuging crude bio-oil

Boap: Water phase; water-like liquid phase formed from adding water to aqueous bio-oil

Boop: Organic bio-oil phase; paste-like precipitate formed from adding water to aqueous bio-oil

SBoap: Aqueous bio-oil phase; organic solvent contacted aqueous bio-oil from organic solvent and combined extractions

SBoop: Organic bio-oil phase; organic solvent contacted organic bio-oil from organic combined and sequential extractions

SolvB: Solvent phase; organic solvent phase after contact with aqueous bio-oil and/or water

NBoap: pH-adjusted aqueous phase; aqueous phase separated after adjusting pH of aqueous bio-oil

NBoop: pH-adjusted organic phase; organic phase separated after adjusting pH of aqueous bio-oil

C16: Hexadecane

C8: Octane

AUTHOR INFORMATION

Corresponding Author

* Email: tsourisc@ornl.gov; Telephone: 865-241-3246; Fax: 865-241-4829

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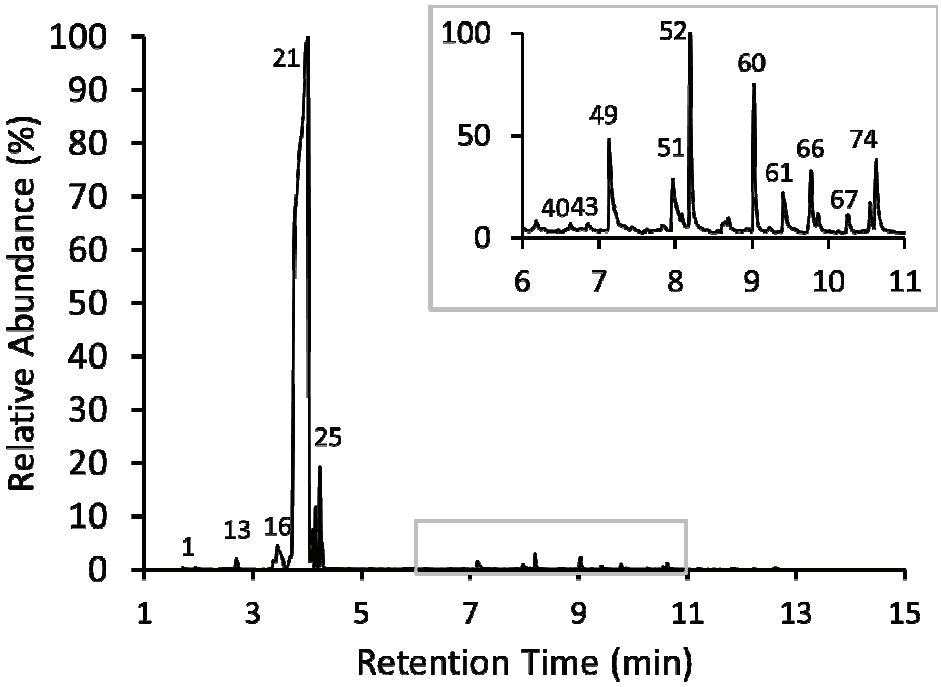
Figure 5. Representative GC-MS analysis of (A) organic phase (NBoop) precipitated and (B) aqueous phase (NBoap) after pH adjustment (pH 5.8).

(A)


Relative Abundance (%)
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52
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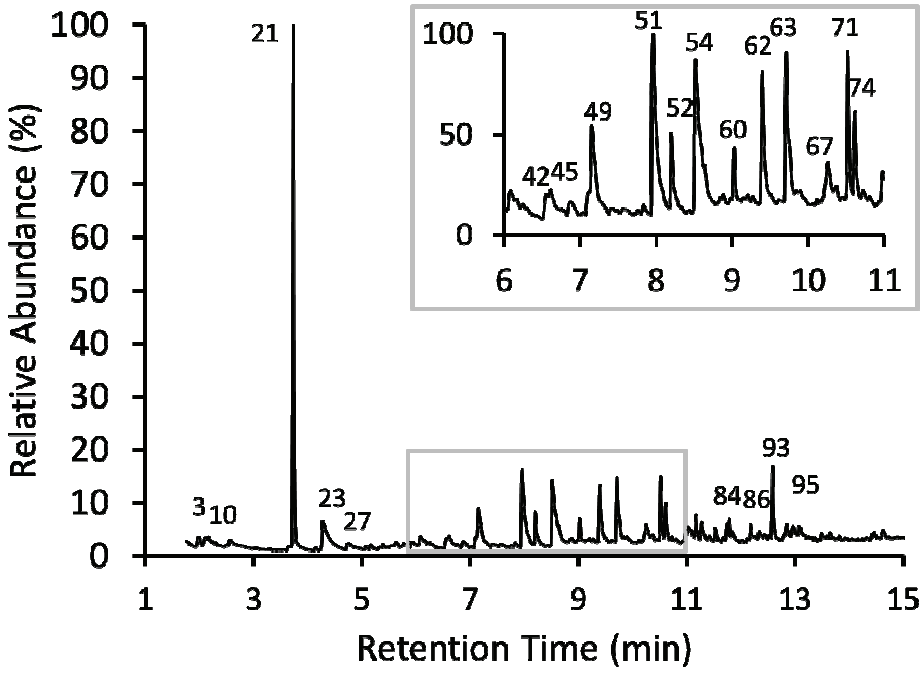
66
67
74

(B)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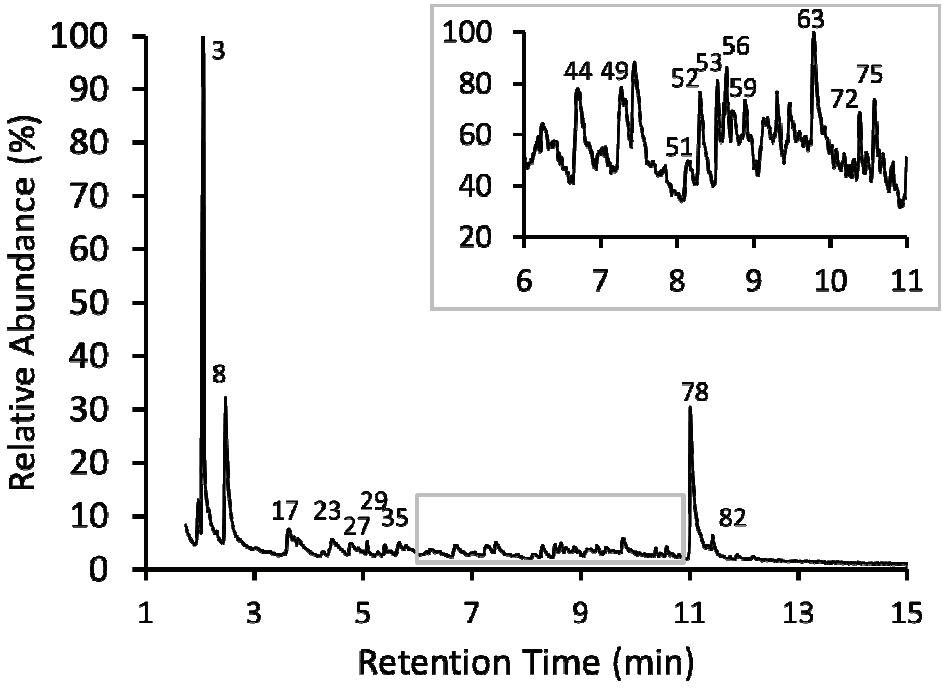
71
74
84
86
93
95

(C)



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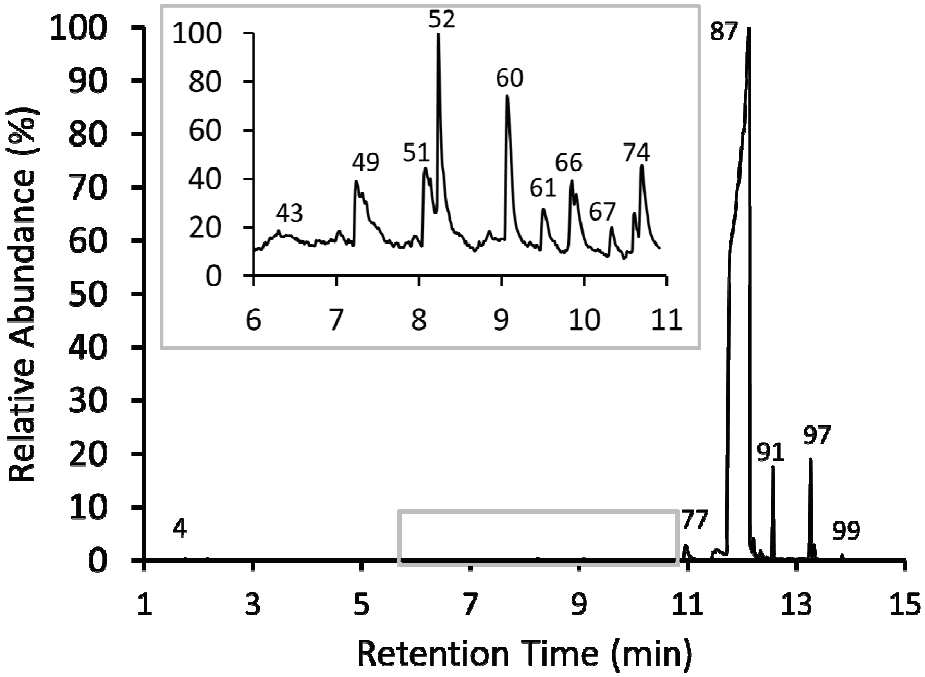
(A)


Relative Abundance (%)
Retention Time (min)
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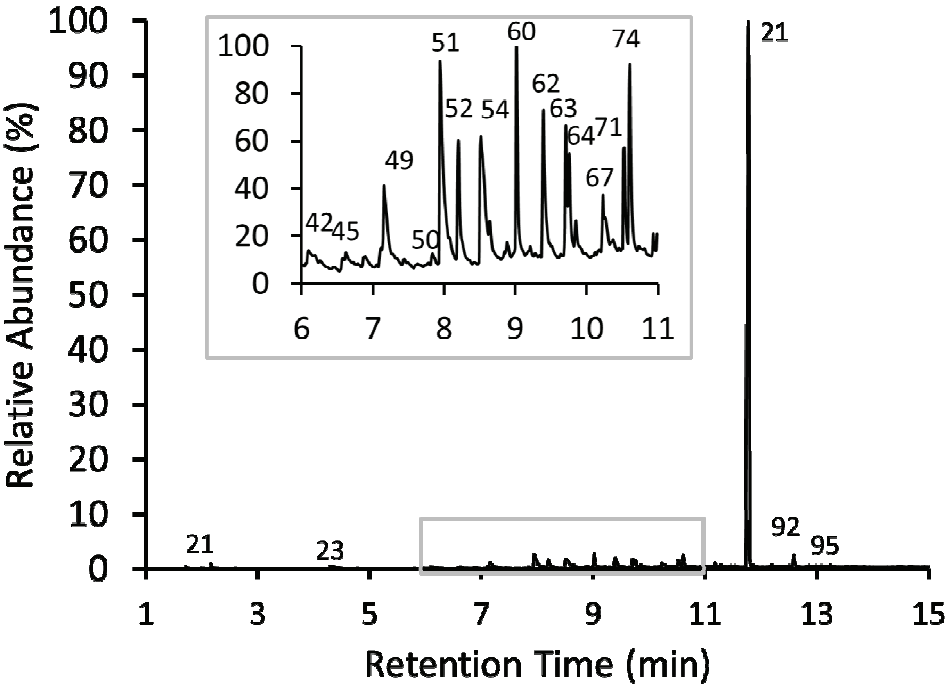
51
52
60
61
66
67
74

(B)


Relative Abundance (%)
Retention Time (min)
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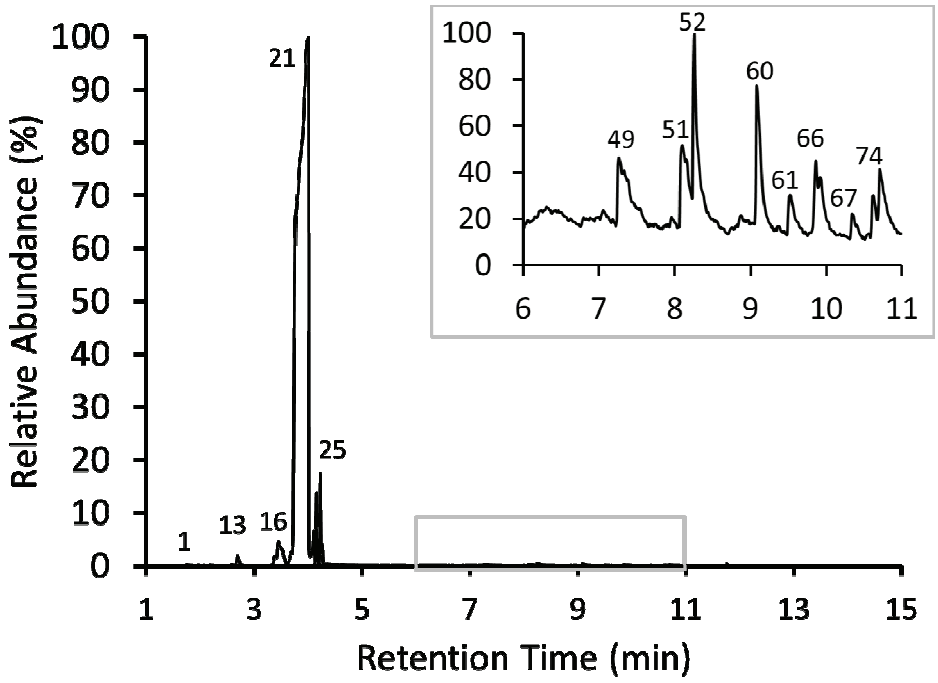
67
71
74

(C)


Relative Abundance (%)
Retention Time (min)
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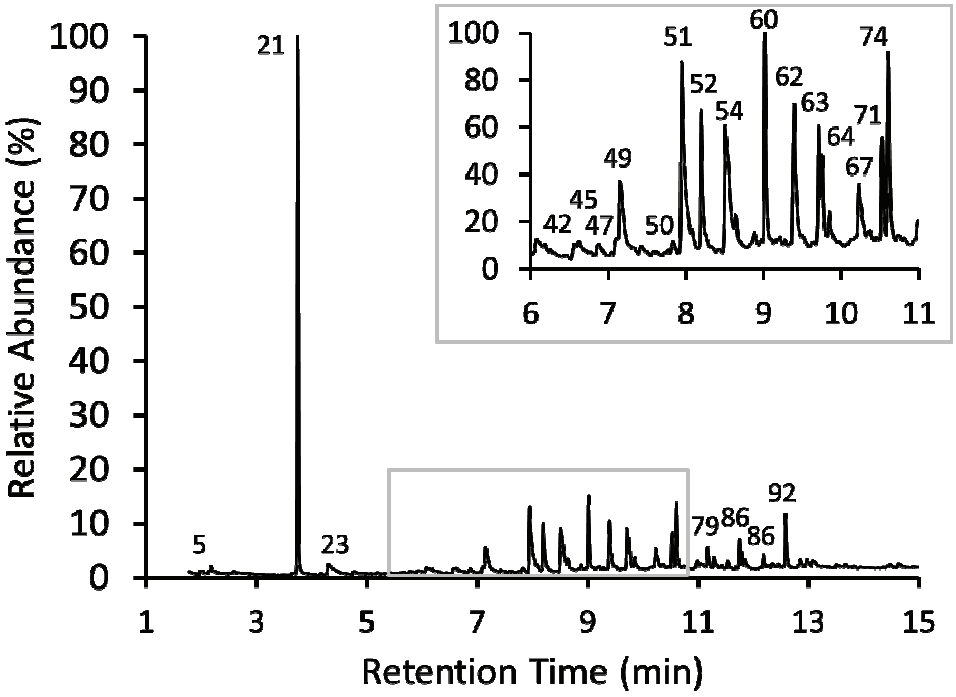
25
49
51
52
60
61
66
67
74

(D)


Relative Abundance (%)
Retention Time (min)
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42
45
47
49
50
51
52
54
60
62
63
64
67
71
74
79
86
86
92

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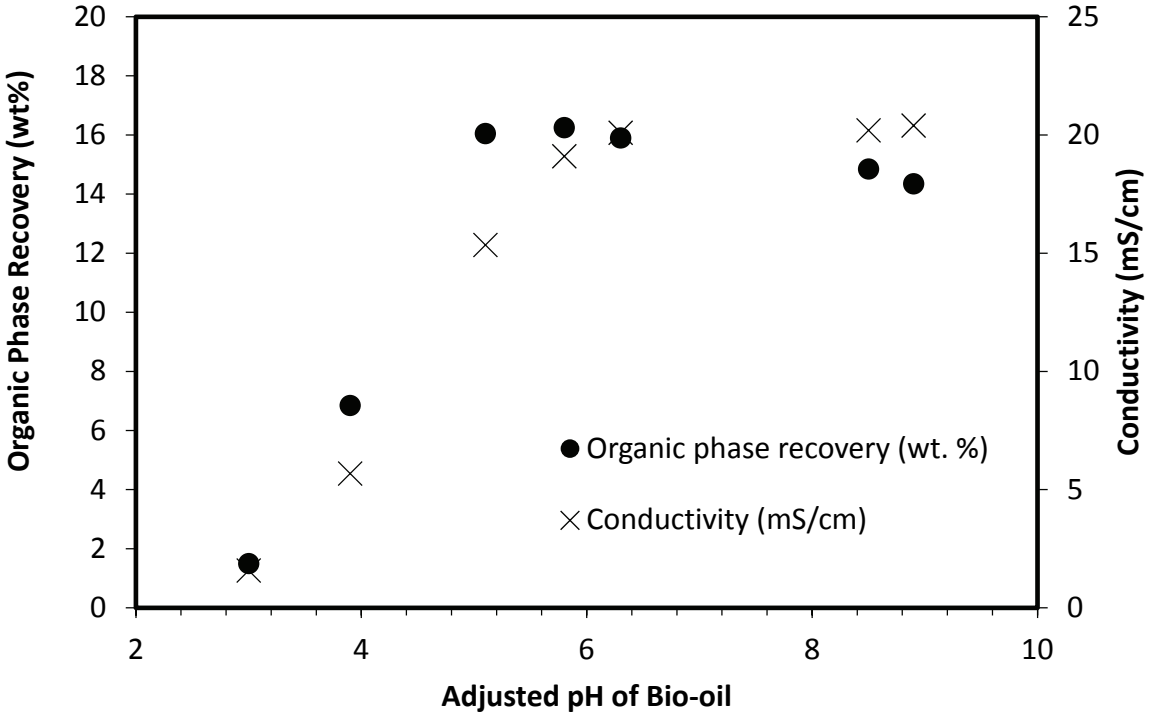

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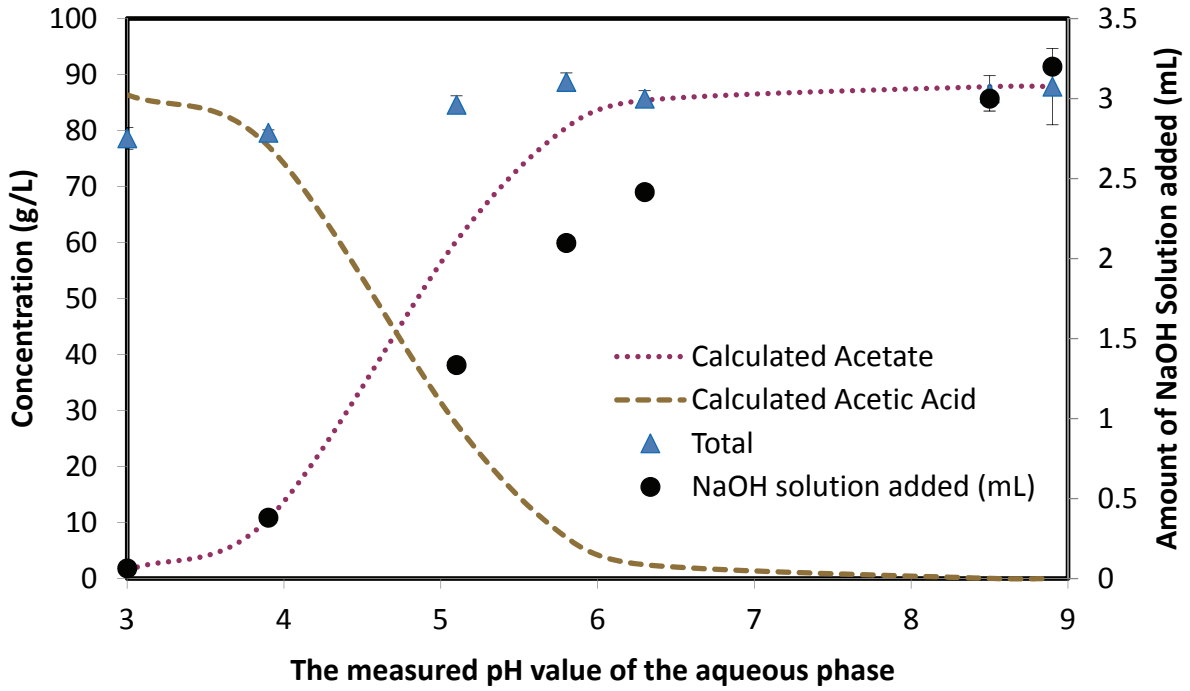

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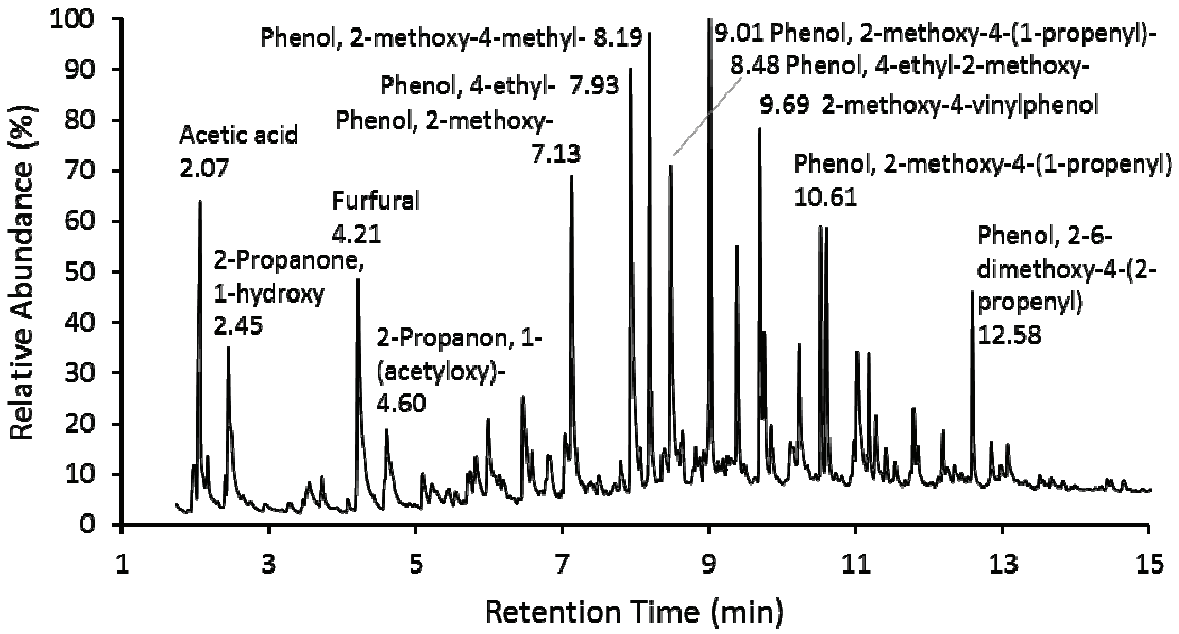
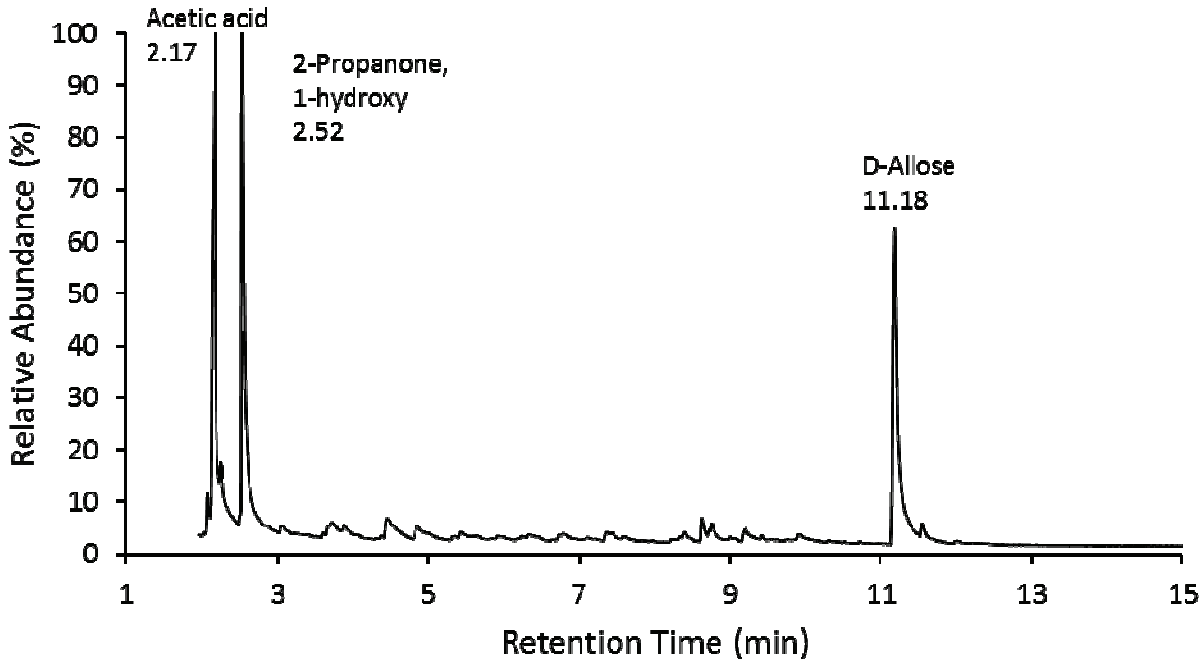
(A)



(B)



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SCHEMES

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Scheme 1. Flow charts for sequential and combined extractions.

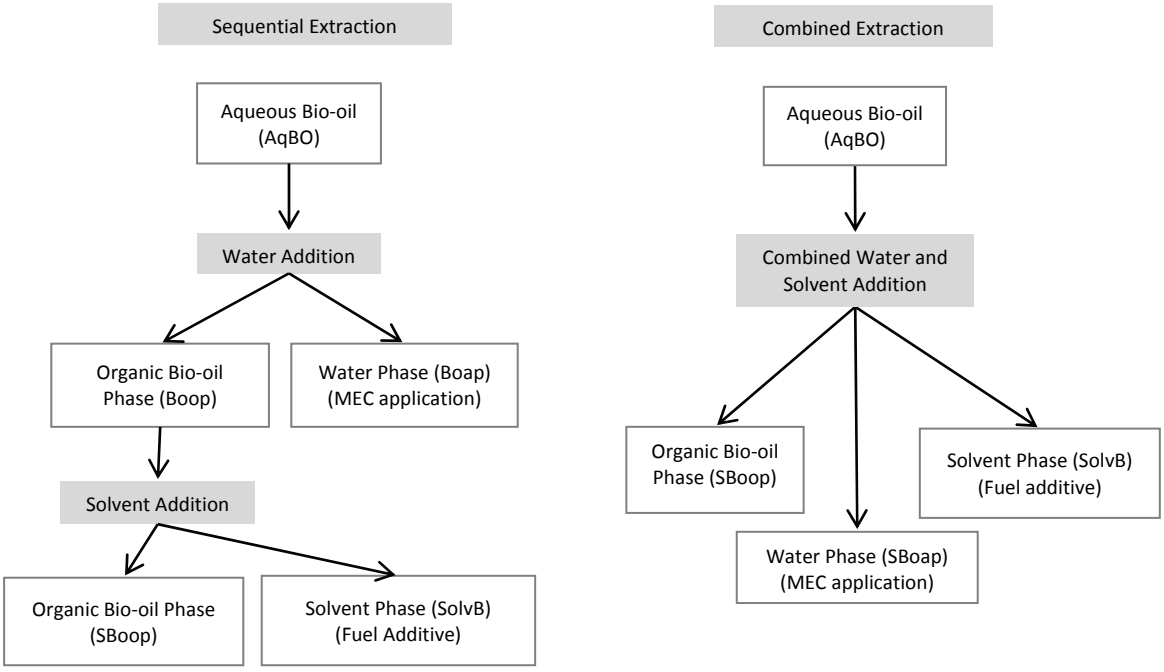
Scheme 2. Mass-balance diagram for the water addition experiment (1:4 wt. ratio of AqBO to water; the mass of water is shown in parentheses)

Scheme 3. Mass-balance diagram for combined extraction with octane (the mass of water is shown in parentheses)

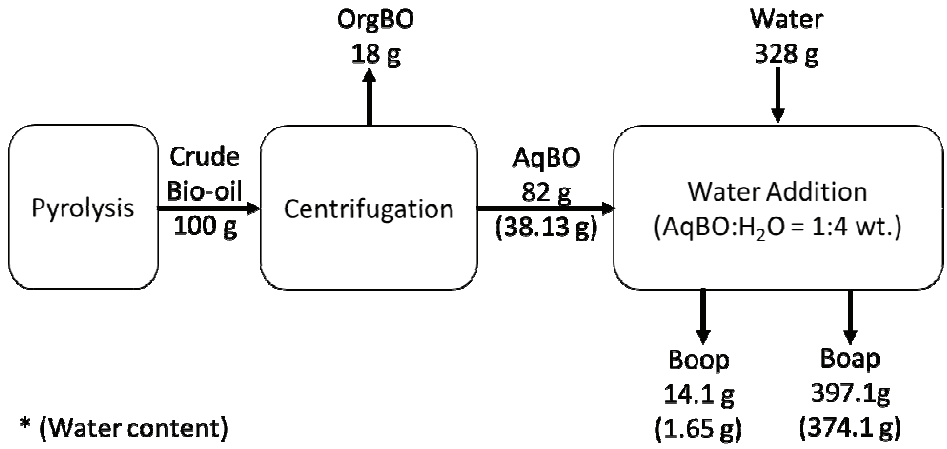
Scheme 4. Mass-balance diagram for sequential extraction with octane (the mass of water is shown in parentheses)

Scheme 5. Mass-balance diagram for pH adjustment (the mass of water is shown in parentheses)

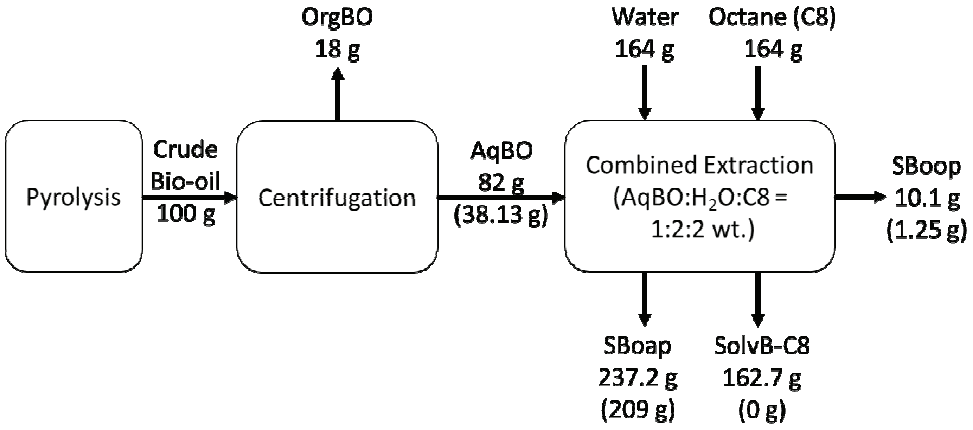
Scheme 1. Flow charts for sequential and combined extractions.



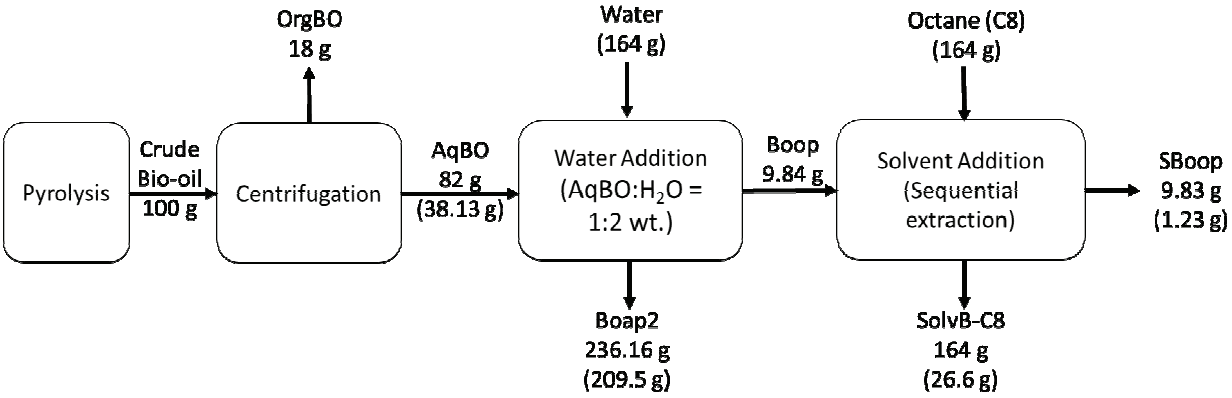
Scheme 2. Mass-balance diagram for the water addition experiment (1:4 wt. ratio of AqBO to water; the mass of water is shown in parentheses)



Scheme 3. Mass-balance diagram for combined extraction with octane (the mass of water is shown in parentheses)



Scheme 4. Mass-balance diagram for sequential extraction with octane (the mass of water is shown in parentheses)



Scheme 5. Mass-balance diagram for pH adjustment (the mass of water is shown in parentheses)

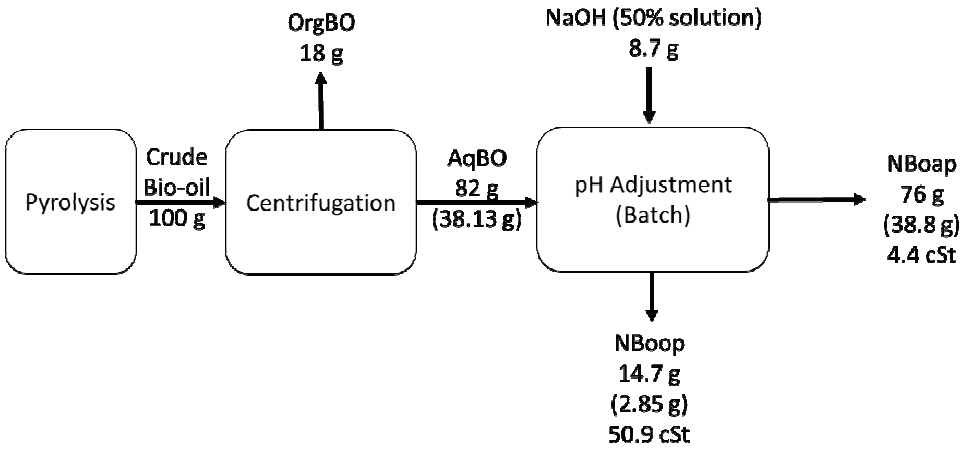


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Table 2. Concentration of acetic acid and relative percentages of types of chemical species present in the samples of each phase and relative percentages of chemical categories excluding alkanes from solvents

Table 3. Changes in the amount of each phase after combined and sequential extraction.

Table 1. Physical properties of switchgass crude bio-oil.

Physical properties	Crude bio-oil
Water content (wt%)	42.3±0.66
Total solid (wt%)	1.7±0.25
pH value	2.8±0.07
Density (g/mL)	1.1±0.001
Ash (wt%)	0.3±0.04
Viscosity at 40 °C (centistokes, cSt)	6.5±0.82
TAN, mg KOH/g	137.4±2.96
Oxygen content of two switchgrass bio-oil batches (wt%)	47.11; 47.5
Heating value (BTU/lb) of centrifuged bio-oil	4,944

Table 2. Concentration of acetic acid, relative percentages of types of chemical species present in the samples of each phase, and relative percentages of chemical categories excluding alkanes from solvents.

Experimental Method			Conc. of acetic acid (g/L)	Chemical Categories (wt%)											
				Acid	Alcohol	Diol	Aldehyde	Ester	Furan	Ketone	Phenolic	Sugar	Ether	Alkane	Others
Water Addition		Boap (1:2 wt.)	19.7	42.4	21.4	0	0	0	5.8	4.2	7.1	17.8	0.7	0	0.8
		Boap (1:4 wt.)	19.6	36	24.5	0	0	0	6.4	7.7	9	14	1.2	0	1.2
		Boop (1:4 wt.)	0.7	1.9	0.6	0.5	0	0	14.4	5.1	74.5	0	0.1	0	2.9
Solvent Extraction	C16	SBoap	20.9	37 41	15.1 16.7	0 0	0 0	0 0	8.5 9.5	4 4.4	7.7 8.6	15.3 16.9	1.2 1.3	9.7 *	1.5 1.6
		SolvB-C16	N/D	0 0	0.6 26.8	0 0	0 0	0 0	0.7 33	0.1 5.9	0.8 34.3	0 0	0 0	97.8 *	0 0
	C8	SBoap	20.8	34.7 37.1	17.3 18.6	0 0	0 0	0 0	4.3 4.6	4.8 5.1	6.4 6.8	23.5 25.2	1.2 1.2	6.7 *	1.2 1.3
		SolvB-C8	N/D	0 0	0 0	0 0	0.1 3.3	0 0	0.1 6.7	0.4 19.4	1.3 70.6	0 0	0 0	98.2 *	0 0
Combined Extraction	C16	SBoap	6.8	35.4 36.1	20.9 21.3	0 0	0 0	0 0	4.9 5	5.4 5.5	8.6 8.8	20.3 20.7	1.4 1.5	1.9 *	1.1 1.2
		SBoop	6.2	11.8 28.9	0.9 2.1	0.5 1	0 0	0 0	5.1 12.5	1.6 4	16.9 41.3	3.3 8	0.1 0.3	59.1 *	0.7 1.7
		SolvB-C16	N/D	0 0	0.4 20.2	0 0	0 0.5	0 0	0.2 12.8	0.1 7.5	1.1 59	0 0	0 0	98.1 *	0 0
	C8	SBoap	5.7	34.9 36	16.5 17	0 0	0 0	0 0	5.5 5.7	5.7 5.9	6.7 6.9	26.1 27	1.4 1.4	3.2 *	0 0
		SBoop	1.3	5.8 7.1	1 1.2	0.6 1	2.9 3.5	0 0	14 17.1	3.1 3.8	51.4 62.7	2.3 2.8	0 0	18 *	0.9 1.1
		SolvB-C8	N/D	0 0	0 0	0 0	0 0	0 0	0 0	0.2 7.4	2 92.6	0 0	0 0	97.9 *	0 0
Sequential Extraction	C16	SBoop	N/D	0.8 3.1	0.2 0.7	0.2 1	0.5 1.8	0 0	3.6 13.6	0.8 3	20.2 75.2	0 0	0 0	73.2 *	0.6 2.2
		SolvB-C16	N/D	0 0	0.4 47.4	0 0	0 5.1	0 0	0 5.7	0 3.1	0.3 38.8	0 0	0 0	99.2 *	0 0
	C8	SBoop	N/D	0.2 0.2	0.5 0.7	0.4 1	1.6 2.2	0 0	9.8 13.3	2.3 3.1	56.5 76.5	0.9 1.2	0 0	26.2 *	1.7 2.3
		SolvB-C8	N/D	0 0	0 0	0 0	0 0	0 0	0 2.4	0 3.1	0.6 94.5	0 0	0 0	99.4 *	0 0

* Notes: The top percentage value of chemical category in the solvent extraction experiment includes alkanes whereas the bottom value was calculated excluding alkanes from organic solvents. C16: hexadecane; C8: octane; N/D: not detected.

Table 3. Changes in the amount of each phase after combined and sequential extraction.

Combined Extraction	SBoap	SolvB-C16	SBoop	SBoap	SolvB-C8	SBoop
Initial amount (g)	14	14	7	14	14	7
Final amount (g)	20.23	13.92	0.85	20.25	13.89	0.86
Percent change (%)	45	-1	-88	45	-1	-88
Sequential Extraction	Boap	SolvB-C16	SBoop	Boap	SolvB-C8	SBoop
Initial amount (g)	14	14.04	7	14	14	7
Final amount (g)	20.29	14.06	0.79	20.16	14.01	0.84
Percent change (%)	45	0	-89	44	0	-88

ASSOCIATED CONTENT

Supporting Information

Figure S1. Schematic of an auger pyrolysis system using switchgrass to produce bio-oil.

Figure S2. (A) Chromatogram of aqueous phase (Boap) from a water addition experiment. (B) Chromatogram of organic phase (Boop) from a water-addition experiment.

Figure S3. (A) Chromatogram of the hexadecane phase (SolvB-C16) after organic solvent extraction of AqBO. (B) Chromatogram of bio-oil phase (SBoap) after contact with hexadecane. (C) Chromatogram of octane phase (SolvB-C8) after solvent extraction of aqueous bio-oil. (D) Chromatogram of bio-oil phase (SBoap) after contact with octane.

Figure S4. Chromatograms of (A) hexadecane (SolvB-C16) phase, (B) organic bio-oil phase (SBoop), and (C) water phase (SBoap) from combined extraction.

Table S1. Water addition ratio used in experiments and the amount of each phase after contacting aqueous bio-oil with water.

Table S2. Chemical species identified in GC-MS analysis.

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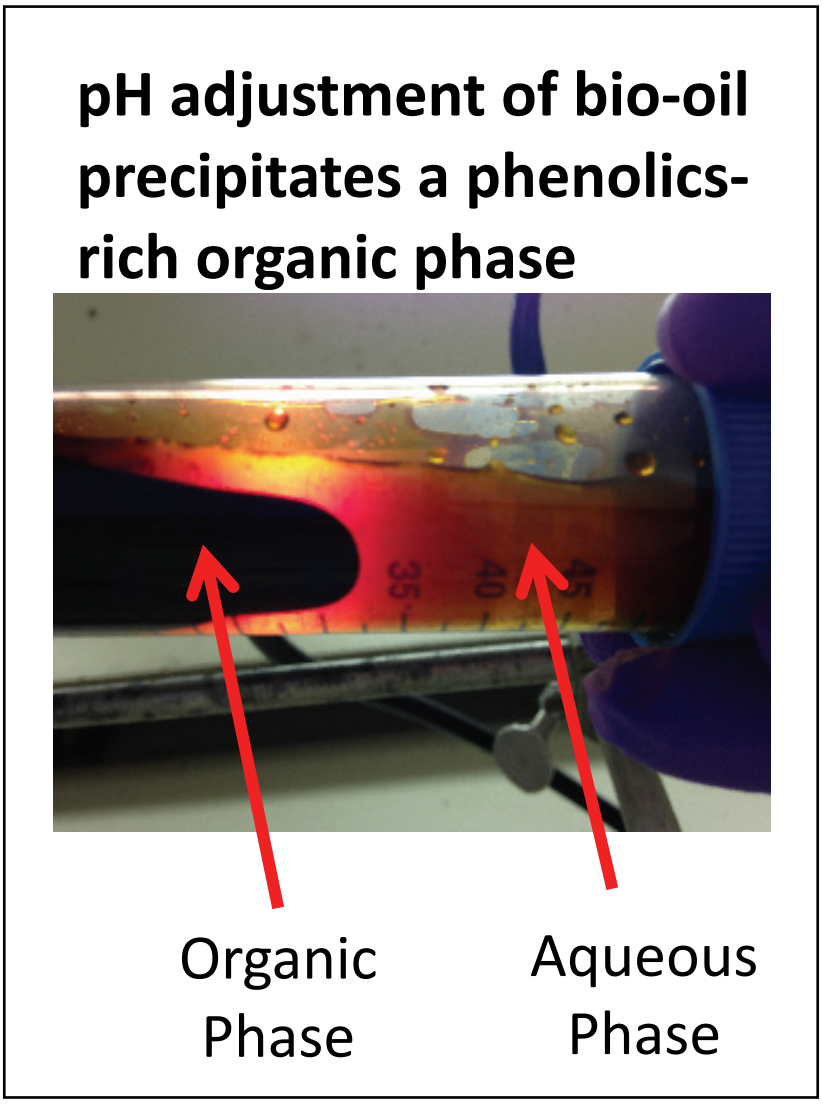
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