

CONTINUOUS AND SCALABLE PROCESSING OF FAST PYROLYSIS OIL TO YIELD A HEAVY AROMATIC FRACTION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Patent Application No. 63/521,060 filed on June 14, 2023, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This invention relates to fractionating fast pyrolysis oil (FPO) from lignocellulosic biomass quantitatively into energy dense streams (e.g., a heavy aromatic fraction and a water-soluble organic fraction), and a comprehensive upgrading approach for recovering value-added products (e.g., precursors for fuel range hydrocarbons, fuel oils, fuel additives, and fuel blends; concentrated fermentable sugars; industrial solvents, and chemicals).

BACKGROUND

[0003] Pyrolysis oil (FPO) is a liquid product produced from fast pyrolysis of biomass. In the fast pyrolysis process, biomass is rapidly heated to 450-550°C in the absence of oxygen and with a short residence time, and rapidly quenched to produce FPO in the form of a condensate. Depending on the process conditions and the condensation train, FPO can either be a single phase mixture or a two-phase mixture with a heavy aromatic fraction (HAF) and a water-soluble organic fraction (WSOF).

SUMMARY

[0004] In a first general aspect, a system for separating a heavy aromatic fraction from fast pyrolysis oil includes a mixing system having a feedstock inlet and configured to accept recycled downstream water and solvent. A separator is coupled to the mixing system. A liquid-liquid extractor is coupled to the separator. A collector vessel is coupled to the separator and configured to accept an input stream from the liquid-liquid extractor. A solvent stripping column is coupled to the collector vessel. A distillation column is coupled to the solvent stripping column. An evaporator is configured to accept an aqueous raffinate from the liquid-liquid extractor. The distillation column is configured to accept an overhead from the solvent stripping column and from the evaporator. In some cases, the separator is configured to provide a heavy aromatic fraction and water-soluble organic fraction by

solvent-aided emulsion inversion. In certain cases, the collector is configured to accept an aqueous raffinate from the liquid-liquid extractor.

[0005] In a second general aspect, producing a heavy aromatic fraction from fast pyrolysis oil includes combining fast pyrolysis oil and a first solvent to yield an emulsion; heating the emulsion to yield an organic phase and an aqueous phase; vapor stripping the organic phase with a second solvent to yield the heavy aromatic fraction and a condensate comprising the first solvent, the second solvent, and water; concentrating the aqueous phase to yield a water-soluble organic fraction, water, and light ends comprising organic compounds having 1-6 carbon atoms; combining the condensate with the light ends to yield a mixture; distilling the mixture to yield a first stream comprising the first solvent and water and a second stream comprising the second solvent; combining the first stream with the fast pyrolysis oil to yield the emulsion; and combining the second stream with the organic phase to yield the heavy aromatic fraction and the condensate.

[0006] The details of one or more embodiments of the subject matter of this disclosure are set forth in the accompanying drawings and the description. Other features, aspects, and advantages of the subject matter will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a block flow diagram of a system and process for preparing a heavy aromatic fraction (HAF) and a water-soluble organic fraction (WSOF) from fast pyrolysis oil (FPO).

DETAILED DESCRIPTION

[0008] Fast pyrolysis oil (FPO) as a fuel has many environmental advantages when compared to fossil fuels. For example, combustion of FPO yields negligible quantities of SO_x and half of the NO_x of fossil fuel combustion, and is also CO₂ neutral. However, the large-scale use of FPO as a liquid fuel can be limited because of its high acidity and thermal instability. Furthermore, FPO has a high water content (e.g., 25-30%), high oxygen content (e.g., 40-50%), is immiscible with fossil fuels, and undergoes phase separation and an increase in viscosity during prolonged storage (aging).

[0009] FPO is a complex mixture containing various kinds of oxygenated organics (e.g., acids, aldehydes, alcohols, phenols, phenolic lignin-derivatives, anhydrosugars, and others with multiple functional groups). These oxygen containing organic compounds can make

FPO unstable, corrosive, and incompatible with conventional fuel and directly affect its commercial applications. Therefore, FPO is typically upgraded before it can be used as a viable renewable fuel in current infrastructure to replace or to blend with petroleum sources.

[0010] Upgrading of FPO is undertaken before it can be used as a substitute for fossil fuels or used for any other purposes. Several FPO upgrading technologies have been proposed to improve the product properties and to increase the range of possible applications. Major upgrading technologies include hydrodeoxygenation (HDO) and hydrocracking. Hydrogen consumption is very high for both these technologies, which in turn affects the scale up and economics of the processes. It has become customary to hydroprocess FPO by utilizing a two-stage approach in which the first stage comprises a hydrotreating stage operating at a mild temperature ($< 300^{\circ}\text{C}$) for the reaction. This first stage reduces the polymerization of FPO that occurs when raw FPO is subjected to temperatures $> 100^{\circ}\text{C}$. Hydrocracking the lightly hydrotreated product is then achieved in a second stage reaction at higher temperature ($> 350^{\circ}\text{C}$). The second stage hydroprocessing method usually requires two reactors, thereby increasing the capital cost of the hydroprocessing technology; more reaction time can also be needed, thereby increasing variable costs. Even without the considerations of high hydrogen consumption, these technologies face challenges in terms of corrosion, catalyst fouling, catalyst stability, catalyst lifetime, and product selectivity.

[0011] In some cases, chemical upgrading of FPO has been achieved by esterification with alcohol (e.g., ethanol and butanol) at mild conditions using mineral acid catalysts (e.g., sulfuric acid and/or various heterogeneous catalysts including resin acid catalysts). The organic acids and aldehydes can be converted by reactions with alcohols to esters and acetals, respectively. The product from the above-mentioned process with different catalysts contains high amounts of water and alcohol and has a low calorific value. Undesirable properties of FPO can be correlated with certain types of compounds. For example, acids contribute to the corrosiveness of FPO, and the instability of FPO is typically caused by the aldehydes, ketones, and phenols. Hence acids, aldehydes, ketones, and phenols are advantageously suppressed in the final product.

[0012] Oxygenates with furanic rings are likely to form coke with aldehydes because of their thermal instability. These precursors can react on the catalytic surfaces and fill up pores, contributing to inactivation of the catalyst during the upgrading and hydrodeoxygenation processing of FPO. Small aldehyde molecules can be condensed together with aromatics to form polymers. Although increasing the hydrogen pressure and reaction temperature while

reducing the acidity of the catalyst can drive down coking on the catalyst surface, minimizing the hydrogen consumption and coking at mild conditions can be challenging.

[0013] Effective separation of pyrolytic sugars and phenolic oligomers offers an array of industrial opportunities and to improve the quality of the FPO for further processing.

Pyrolytic sugars can be useful for direct upgrading to liquid transportation fuels and/or fermentation to corresponding alcohols. Phenolic oligomers have potential to be used in various applications that include resins, binders, asphalt, coatings, adhesives, aromatic chemicals, unique polymers, and the production of fuels and preservatives.

[0014] Processes described herein are designed to separate highly reactive components in FPO, which have potential to plug hydrotreaters, into an aqueous phase and convert the remaining organic components into hydrocarbons. The fractionation of FPO as described herein removes water and reduces the concentration of aldehydes, sugars, acids, and metals in the organic phase referred to herein as the heavy aromatic fraction (HAF). Table 1 lists properties of this HAF compared to commercially available FPO from wood. The resulting HAF enables downstream distillate hydroprocessing with high biomass-to-biofuel carbon yields using commercially available sulfided, base-metal catalysts.

Table 1. Improved properties of the fast pyrolysis oil heavy aromatic fraction described herein compared to commercially available fast pyrolysis oil (FPO).

Component	Unit	Typical Wood FPO	Typical HAF	Change (%)
Water	W _{H2O} (%)	25	< 1	> - 90
Oxygen	W _O (%)	47	28-30	-35
Higher Heating Value	MJ/kg	17	25-27	60
Glycolaldehyde	WC _{2H4O2} %	6-8	~2	-70
Levogluconan	WC _{6H10O5} (%)	3-5	~1	- 60 to - 80
Acetic acid	WCH _{3COOH} %	3-4	1-2	-60
Metals	mg/kg	50 > 1000	< 10 - 50	-90

[0015] FPO is an oil-in-water microemulsion in which pyrolytic lignin fragments are held together by small polar molecules, herein collectively referred to as the “heavy aromatic fraction” (HAF) in the presence of water and pyrolytic cellulose/hemicellulose fragments. Processes described herein leverage the emulsion behavior of FPO by using a hydrophobic organic solvent and water in a solvent/anti-solvent process. When water and hydrophobic organic solvent are added sequentially, the solvent expels water and small oxygenates from

the HAF to produce solvated pyrolytic lignin that is less dense than the aqueous phase that includes water, pyrolytic sugars, and small oxygenates. Moreover, unlike conventional solvent extraction processes, which depend on the solubility of lignin in the solvent, this emulsion-destabilizing process typically requires much smaller quantities of solvent.

[0016] As defined in ASTM D7544-23 Standard Specification for Pyrolysis Liquid Biofuel, FPO is a single-phase material. This single-phase material has about 25 % mass fraction of water embodied in what is recognized to be an emulsion. The remainder of the material includes water-soluble small molecules, such as acetic acid, acetol, glycolaldehyde, anhydrosugar, anhydrosugar polymers derived from the cellulose, and a hydrophobic aromatic fraction (HAF) derived from the lignin and the cellulose breakdown. Often the HAF is described as “pyrolytic lignin”, which is typically understood to describe the precipitate that results when FPO is combined with cold water.

[0017] A quantity of pyrolytic lignin can be assessed by combining FPO with an equal mass of water to obtain a raw precipitate. This precipitate typically has about 50% of the initial mass of the FPO. However, the precipitate, which is typically contaminated with other materials from the FPO, can be re-dissolved in methanol (e.g., an equal mass of methanol) to yield a mixture. Water (e.g., another equal mass) can be combined with this mixture, to precipitate a purified pyrolytic lignin from which the methanol can then be evaporated.

[0018] The main phase of a FPO emulsion includes aggregates of lignin-derived molecules, and the dispersed phase is believed to include water and water-soluble molecules. The aggregates tend to grow with aging and are typically the equivalent volume of 4 coniferyl alcohol C-9 lignin units (typically called G-Lignin, based on the guaiacyl OH and methoxy substituents in the ring). The molecular weight of 4G-lignin (tetramer lignin) is approximately 700 – 750 g/mol.

[0019] As FPO ages, chemical reactions take place that result in the production of water, some cross-linking of small molecules, and agglomeration of the tetramer units into larger units (e.g., based on electrostatic interactions), resulting in phase separation as these aggregates fall out of solution. The pyrolytic lignin is believed to be held together using co-solvent molecules, in a loose network which solubilizes the water and water-soluble organics. The co-solvent molecules are typically small organic molecules (C1-C6) with a polar group (e.g., -OH, >C=O, -COOH) and a non-polar hydrocarbon or aromatic “body.” The water-soluble phase holds most of the water, and the organic molecules that are highly polar (e.g., sugars including anhydrosugars such as levoglucosan and polyols or sugar oligomers). This emulsion can be destabilized by increasing the water to water-soluble organic ratio, such that

the water-insoluble tetramer lignin separates, and then adding a co-solvent back to the freshly phase separated material such that a single uniform phase is formed.

[0020] The single-phase FPO exists as a Type IV Winsor emulsion. In this case, the HAF (pyrolytic lignin) is behaving as a surfactant as well as an oil normally immiscible in water, while the polar organics are in an aqueous solution referred to herein as the water-soluble organic fraction (WSOF). On increasing the water concentration, the HAF forms a bottom phase on account of its density, and the WSOF forms an upper phase of mainly water and water-soluble polar materials. That is, a Winsor Type II emulsion is created.

[0021] A Type I Winsor emulsion, which can be created by adding a lipophilic polar solvent, has Hansen solubility parameters in the range (Dispersion 8 - 10 MPa^{0.5}, Polar 2 - 3 MPa^{0.5}, and Hydrogen Bonding in the range of 2 - 4.5 MPa^{0.5}). Only a small amount of the lipophilic polar solvent is needed if the Winsor Type IV emulsion is close to the critical point of converting to a Winsor Type I emulsion. Then only a small amount of additional water as anti-solvent will trigger the formation of the Type I emulsion with an aqueous phase containing most of the sugar and WSOF, and a solvent phase containing the HAF.

[0022] For recovery of the HAF, the very concentrated solution in the lipophilic polar solvent can be extracted from a small volume of distilled water. After drying the solvent phase, the residual heavy oil can be recovered by evaporation of the solvent. The combined water phase can be extracted with organic solvents and subsequently distilled to produce clean fractions of pyrolytic sugars and phenolic monomers. Further, these phenolic monomers can be added back to the HAF fraction for the future upgrading purposes.

[0023] Using the Winsor emulsion behavior, the additional volumes of solvent and water are minimized. A flow diagram of the process is shown in FIG. 1. To the FPO, organic solvent is added at first and mixed vigorously (e.g., for about 1 to 30 minutes at temperature of ambient to 60°C) in a batch, semicontinuous, or continuous process using an overhead or static mixing unit 100. To this mixture, water is added and mixed vigorously (e.g., for about 1 to 30 minutes at temperature of ambient to 60°C) in a batch, semicontinuous, or continuous process using an overhead or static mixing unit. After settling the mixture (e.g., for about 1 to 90 minutes) in separator 200, a clear, distinct phase separation is achieved between a top organic phase and a bottom aqueous phase. The organic phase is sent to a combiner unit 400 and the aqueous phase is sent to an optional liquid-liquid-extraction (LLE) unit 300. In the LLE unit, solvent (fresh, recycled, or both) is used to extract residual HAF organics from the aqueous phase. If LLE is utilized, the extracted organics are sent to the combiner unit 400 and the resulting raffinate is sent to the concentration unit 500. In the concentration unit 500,

excess water and volatile organics are removed from the aqueous mixture with heat with or without the presence of vacuum, or by membrane processing, to produce a WSOF with a water mass fraction of about 20-30 %. Further, the organic streams collected from the combiner unit are sent to a solvent stripping unit 700, and there combined with ethanol (e.g., 1% to 25% mass fraction). Vacuum and heat are applied to distill off the solvent, water, and ethanol, yielding the HAF. The ethanol, water, solvent mixture is sent to alcohol stream stripping unit to recover and recycle the water, solvent, and ethanol.

[0024] A system for separating a HAF from FPO includes a mixing system having a feedstock inlet and configured to accept recycled downstream water and solvent. A separator is coupled to the mixing system. A liquid-liquid extractor is coupled to the separator. A collector vessel is coupled to the separator and configured to accept an input stream from the liquid-liquid extractor. A solvent stripping column is coupled to the collector vessel. A distillation column is coupled to the solvent stripping column. An evaporator is configured to accept an aqueous raffinate from the liquid-liquid extractor. The distillation column is configured to accept an overhead from the solvent stripping column and from the evaporator. In some cases, the separator is configured to provide a HAF and a WSOF by solvent-aided emulsion inversion. In certain cases, the collector is configured to accept an aqueous raffinate from the liquid-liquid extractor.

[0025] Producing a HAF from FPO includes combining FPO and a first solvent to yield an emulsion. The first solvent is an organic solvent. Combining the FPO and the first solvent occurs prior to combining the FPO with water or aqueous composition. The emulsion is heated to yield an organic phase and an aqueous phase. The organic phase is vapor stripped with a second solvent to yield the HAF and a condensate comprising the first solvent, the second solvent, and water. The aqueous phase is concentrated to yield a WSOF, water, and light ends comprising organic compounds having 1-6 carbon atoms. The condensate is combined with the light ends to yield a mixture. The mixture is distilled to yield a first stream comprising the first solvent and water and a second stream comprising the second solvent. The first stream is combined with the FPO to yield the emulsion. The second stream is combined with the organic phase to yield the HAF and the condensate.

[0026] The FPO is typically derived from lignocellulosic biomass such as wood, straw, grasses, or any combination thereof. The first solvent comprises a C4-C8 alcohol, a C4-C8 alcohol-derived methyl or ethyl ester, a water-insoluble ketone, or a combination thereof. In one example, the water-insoluble ketone is methyl ethyl ketone, methyl isobutyl ketone, or a combination thereof. The second solvent is typically a C1-C4 alcohol, such as methanol,

ethanol, n-propanol, isopropanol, butanol, or a combination thereof. The HAF includes polymeric, oligomeric, and monomeric aromatic derivatives of lignin. The aqueous phase includes water-soluble organic compounds and water-soluble inorganic compounds from the fast pyrolysis oil.

[0027] The water typically comprises 15 to 30% mass fraction of the FPO. The first solvent typically comprises 1% to 25% mass fraction of the emulsion. The second organic phase typically includes phenolic compounds and neutral compounds..

[0028] Combining FPO and the first solvent before combining water or an aqueous composition with the FPO reduces or eliminates precipitation of HAF. Combining FPO and the first solvent can be achieved by a process such as stirring or static in-line mixing. Combining the FPO and the first solvent occurs at a pressure in a range of atmospheric pressure to about 100 psig. Heating the emulsion occurs in a temperature range of 15°C to 65°C. In one example, the combining occurs at a temperature of about 40°C. The liquid flow regime of the emulsion provides a Reynolds Number between 5 and 1,000,000, with a minimum preferred value of above 200. The temperature, pressure, and flow conditions of the combining and heating are selected such that a total amount of aromatic compounds in the organic phase is at least 80% mass fraction of the total amount of aromatic compounds of the FPO. In other examples, the temperature, pressure, and flow conditions of combining the FPO and the first solvent and of heating the emulsion are selected such that a total amount of aromatic compounds in the organic phase is at least 85% mass fraction of the total amount of aromatic compounds of the FPO or at least 90% mass fraction of the total amount of aromatic compounds of the FPO.

[0029] In some embodiments, water or an aqueous composition (e.g., an aqueous solution) is combined with the FPO after the FPO has been combined with the first solvent (e.g., the water or aqueous composition is combined with the emulsion). In one example, the aqueous composition is recovered from the aqueous phase by distillation and combined with the FPO and the first solvent in a recycling loop (e.g., see “recycled water” in FIG. 1). In this example, the aqueous composition includes acetic acid (e.g., about 2 wt% to about 7 wt%), acetol (e.g., about 1 wt% to about 3 wt%), glycoaldehyde (e.g., about 0.1 wt% to about 1 wt%), or any combination thereof, and can include other low-boiling water-soluble organics that originate from the FPO feedstock.

[0030] Combining the water or aqueous composition with the FPO and the first solvent (e.g., the emulsion) can include stirring or static in-line mixing following addition of the water or aqueous composition to yield a second emulsion, and before settling of the HAF.

Heating the second emulsion occurs at a temperature in a range of 15°C to 65°C. In one example, combining the water or aqueous composition with the FPO and the first solvent (e.g., the emulsion) occurs at a temperature of about 40°C. The liquid flow regime of the mixture of FPO, first solvent, and water or aqueous composition (e.g., the second emulsion) provides a Reynolds Number between 5 and 1,000,000, with a minimum preferred value of above 200.

[0031] In the vapor stripping, a mass fraction of the second solvent to a total amount of the heavy aromatic fraction and the first solvent is in a range of 5% to 20%. The distilling typically occurs at atmospheric pressure, and the concentrating typically occurs at less than atmospheric pressure.

[0032] A total amount of carbon in the heavy aromatic fraction and the water-soluble organic fraction is usually at least 90% or at least 95% of a total amount of carbon in the FPO. A total amount of aromatic compounds in the HAF is usually at least 95% mass fraction of an aromatic content of the FPO. At least 95% mass fraction of pyrolytic sugars in the FPO is typically transferred to the WSOF. At least 80% mass fraction of inorganic compounds in the FPO is transferred to the WSOF. In one example, at least 90% mass fraction of inorganic compounds in the FPO is transferred to the WSOF.

[0033] Certain embodiments include extracting the aqueous phase with an additional amount of the first solvent to yield an additional organic phase and an aqueous raffinate and combining the additional organic phase with the organic phase before vapor stripping the organic phase. Certain embodiments include removing water from the aqueous raffinate to yield a first stream including residual pyrolysis oil and a second stream including water. In some cases, the second stream is a clean water stream. Removing water from the aqueous raffinate can include using a multiple-effect evaporator or a membrane filtration unit.

[0034] Although the disclosed inventive concepts include those defined in the attached claims, it should be understood that the inventive concepts can also be defined in accordance with the following embodiments.

[0035] In addition to the embodiments of the attached claims and the embodiments described above, the following numbered embodiments are also innovative.

[0036] Embodiment 1 is a process for producing a heavy aromatic fraction from fast pyrolysis oil, the process comprising:

- combining fast pyrolysis oil and a first solvent to yield an emulsion;
- heating the emulsion to yield an organic phase and an aqueous phase;

vapor stripping the organic phase with a second solvent to yield the heavy aromatic fraction and a condensate comprising the first solvent, the second solvent, and water;

concentrating the aqueous phase to yield a water-soluble organic fraction, water, and light ends comprising organic compounds having 1-6 carbon atoms;

combining the condensate with the light ends to yield a mixture;

distilling the mixture to yield a first stream comprising the first solvent and water and a second stream comprising the second solvent;

combining the first stream with the fast pyrolysis oil to yield the emulsion; and

combining the second stream with the organic phase to yield the heavy aromatic fraction and the condensate.

[0037] Embodiment 2 is the process of embodiment 1, wherein the fast pyrolysis oil is derived from lignocellulosic biomass comprising wood, straw, grasses, or any combination thereof.

[0038] Embodiment 3 is the process of embodiment 1 or 2, wherein the first solvent comprises a C4-C8 alcohol, a C4-C8 alcohol-derived methyl or ethyl ester, a water-insoluble ketone, or a combination thereof.

[0039] Embodiment 4 is the process of embodiment 3, wherein the water-insoluble ketone comprises methyl ethyl ketone, methyl isobutyl ketone, or a combination thereof.

[0040] Embodiment 5 is the process of any one of embodiments 1-4, wherein the second solvent comprises a C1-C4 alcohol.

[0041] Embodiment 6 is the process of embodiment 5, wherein the second solvent comprises methanol, ethanol, n-propanol, isopropanol, butanol, or a combination thereof.

[0042] Embodiment 7 is the process of any one of embodiments 1-6, wherein the heavy aromatic fraction comprises polymeric, oligomeric, and monomeric aromatic derivatives of lignin.

[0043] Embodiment 8 is the process of any one of embodiments 1-7, wherein the aqueous phase comprises water-soluble organic compounds and water-soluble inorganic compounds from the fast pyrolysis oil.

[0044] Embodiment 9 is the process of any one of embodiments 1-8, wherein combining the fast pyrolysis oil and the first solvent occurs prior to combining water or an aqueous composition with the fast pyrolysis oil.

[0045] Embodiment 10 is the process of any one of embodiments 1-9, wherein combining the fast pyrolysis oil and the first solvent comprises stirring or static in-line mixing.

[0046] Embodiment 11 is the process of any one of embodiments 1-10, wherein combining the fast pyrolysis oil and the first solvent occurs at a pressure in a range of atmospheric pressure to about 100 psig.

[0047] Embodiment 12 is the process of any one of embodiments 1-11, wherein heating the emulsion occurs at a temperature in a range of 15°C to 65°C.

[0048] Embodiment 13 is the process of embodiment 12, wherein heating the emulsion occurs at a temperature of about 40°C.

[0049] Embodiment 14 is the process of any one of embodiments 1-13, wherein the liquid flow regime of the emulsion provides a Reynolds Number between 5 and 1,000,000.

[0050] Embodiment 15 is the process of any one of embodiments 1-14, wherein the temperature, pressure, and flow conditions of combining the fast pyrolysis oil and the first solvent and heating the emulsion are selected such that a total amount of aromatic compounds in the organic phase is at least 80% mass fraction of the total amount of aromatic compounds of the fast pyrolysis oil.

[0051] Embodiment 16 is the process of any one of embodiments 1-15, wherein the water comprises 15% to 35% mass fraction of the emulsion.

[0052] Embodiment 17 is the process of any one of embodiments 1-16, wherein the first solvent comprises 1% to 25% mass fraction of the emulsion.

[0053] Embodiment 18 is the process of any one of embodiments 1-17, wherein the second organic phase comprises phenolic compounds and neutral compounds.

[0054] Embodiment 19 is the process of any one of embodiments 1-18, wherein, in the vapor stripping, a mass fraction of the second solvent to a total amount of the heavy aromatic fraction and the first solvent is in a range of 5% to 20%.

[0055] Embodiment 20 is the process of any one of embodiments 1-19, wherein the distilling occurs at atmospheric pressure.

[0056] Embodiment 21 is the process of any one of embodiments 1-20, wherein the concentrating occurs at a pressure less than atmospheric pressure.

[0057] Embodiment 22 is the process of any one of embodiments 1-21, wherein a total amount of carbon in the heavy aromatic fraction and the water-soluble organic fraction comprises at least 90% or at least 95% of a total amount of carbon in the fast pyrolysis oil.

[0058] Embodiment 23 is the process of any one of embodiments 1-22, wherein a total amount of aromatic compounds in the heavy aromatic fraction is at least 95% mass fraction of an aromatic content of the fast pyrolysis oil.

[0059] Embodiment 24 is the process of any one of embodiments 1-23, wherein at least 95% mass fraction of pyrolytic sugars in the fast pyrolysis oil is transferred to the water-soluble organic fraction.

[0060] Embodiment 25 is the process of any one of embodiments 1-24, wherein at least 80% mass fraction of inorganic compounds in the fast pyrolysis oil is transferred to the water-soluble organic fraction.

[0061] Embodiment 26 is the process of any one of embodiments 1-25, further comprising combining water or an aqueous composition with the emulsion to yield a second emulsion.

[0062] Embodiment 27 is the process of any one of embodiments 1-26, wherein combining the water or the aqueous composition with the emulsion comprises stirring or static in-line mixing.

[0063] Embodiment 28 is the process of embodiment 26 or 27, wherein combining the water or the aqueous composition with the emulsion occurs at a pressure in a range of atmospheric pressure to about 100 psig.

[0064] Embodiment 29 is the process of any one of embodiments 26-28, wherein the liquid flow regime of the second emulsion provides a Reynolds Number between 5 and 1,000,000.

[0065] Embodiment 30 is the process of any one of embodiments 26-29, wherein heating the emulsion comprises heating the second emulsion, and heating the second emulsion occurs at a temperature in a range of 15°C to 65°C.

[0066] Embodiment 31 is the process of embodiment 30, wherein heating the second emulsion occurs at a temperature of about 40°C.

[0067] Embodiment 32 is the process of any one of embodiments 26-31, wherein the temperature, pressure, and flow conditions of combining the emulsion and the water or aqueous composition and heating the second emulsion are selected such that a total amount of aromatic compounds in the organic phase is at least 80% mass fraction of the total amount of aromatic compounds of the fast pyrolysis oil.

[0068] Embodiment 33 is the process of any one of embodiments 1-32, further comprising:

extracting the aqueous phase with an additional amount of the first solvent to yield an additional organic phase and an aqueous raffinate; and

combining the additional organic phase with the organic phase before vapor stripping the organic phase.

[0069] Embodiment 34 is the process of embodiment 33, further comprising removing water from the aqueous raffinate to yield a first stream comprising residual pyrolysis oil and a second stream comprising water.

[0070] Embodiment 35 is the process of embodiment 34, wherein the second stream is a clean water stream.

[0071] Embodiment 36 is the process of embodiment 34, wherein the second stream comprises water-soluble organic compounds.

[0072] Embodiment 37 is the process of embodiment 36, wherein the water-soluble organic compounds comprise acetic acid, acetol, glycoaldehyde, or any combination thereof.

[0073] Embodiment 38 is the process of embodiment 37, wherein the second stream comprises about 2 wt% to about 7 wt% acetic acid.

[0074] Embodiment 39 is the process of embodiment 37 or 38, wherein the second stream comprises about 1 wt% to about 3 wt% acetol.

[0075] Embodiment 40 is the process of any one of embodiments 37-39, wherein the second stream comprises about 0.1 wt% to about 1 wt% glycoaldehyde.

[0076] Embodiment 41 is the process of any one of embodiments 34-40, further comprising combining the second stream with the emulsion in a recycle loop.

[0077] Embodiment 42 is the process of embodiments 41, wherein combining the second stream with the emulsion occurs before heating the emulsion.

[0078] Embodiment 43 is the process of any one of embodiments 34-42, wherein removing water from the aqueous raffinate comprises using a multiple-effect evaporator or a membrane filtration unit.

[0079] Embodiment 44 is a system for separating a heavy aromatic fraction from fast pyrolysis oil, the system comprising:

- a mixing system comprising a feedstock inlet and configured to accept recycled downstream water and solvent;
- a separator coupled to the mixing system;
- a liquid-liquid extractor coupled to the separator;
- a collector vessel coupled to the separator and configured to accept an input stream from the liquid-liquid extractor;
- a solvent stripping column coupled to the collector vessel;
- a distillation column coupled to the solvent stripping column; and
- an evaporator configured to accept an aqueous raffinate from the liquid-liquid extractor,

wherein the distillation column is configured to accept an overhead from the solvent stripping column and from the evaporator.

[0080] Embodiment 45 is the system of embodiment 44, wherein the separator is configured to provide a heavy aromatic fraction and water-soluble organic fraction by solvent-aided emulsion inversion.

[0081] Embodiment 46 is the system of embodiment 44 or 45, wherein the collector is configured to accept an aqueous raffinate from the liquid-liquid extractor.

[0082] Although this disclosure contains many specific embodiment details, these should not be construed as limitations on the scope of the subject matter or on the scope of what may be claimed, but rather as descriptions of features that may be specific to particular embodiments. Certain features that are described in this disclosure in the context of separate embodiments can also be implemented, in combination, in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple embodiments, separately, or in any suitable sub-combination. Moreover, although previously described features may be described as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can, in some cases, be excised from the combination, and the claimed combination may be directed to a sub-combination or variation of a sub-combination.

[0083] Particular embodiments of the subject matter have been described. Other embodiments, alterations, and permutations of the described embodiments are within the scope of the following claims as will be apparent to those skilled in the art. While operations are depicted in the drawings or claims in a particular order, this should not be understood as requiring that such operations be performed in the particular order shown or in sequential order, or that all illustrated operations be performed (some operations may be considered optional), to achieve desirable results.

[0084] Accordingly, the previously described example embodiments do not define or constrain this disclosure. Other changes, substitutions, and alterations are also possible without departing from the spirit and scope of this disclosure.

WHAT IS CLAIMED IS:

1. A process for producing a heavy aromatic fraction from fast pyrolysis oil, the process comprising:
 - combining fast pyrolysis oil and a first solvent to yield an emulsion;
 - heating the emulsion to yield an organic phase and an aqueous phase;
 - vapor stripping the organic phase with a second solvent to yield the heavy aromatic fraction and a condensate comprising the first solvent, the second solvent, and water;
 - concentrating the aqueous phase to yield a water-soluble organic fraction, water, and light ends comprising organic compounds having 1-6 carbon atoms;
 - combining the condensate with the light ends to yield a mixture;
 - distilling the mixture to yield a first stream comprising the first solvent and water and a second stream comprising the second solvent;
 - combining the first stream with the fast pyrolysis oil to yield the emulsion; and
 - combining the second stream with the organic phase to yield the heavy aromatic fraction and the condensate.
2. The process of claim 1, wherein the fast pyrolysis oil is derived from lignocellulosic biomass comprising wood, straw, grasses, or any combination thereof.
3. The process of claim 1, wherein the first solvent comprises a C4-C8 alcohol, a C4-C8 alcohol-derived methyl or ethyl ester, a water-insoluble ketone, or a combination thereof.
4. The process of claim 3, wherein the water-insoluble ketone comprises methyl ethyl ketone, methyl isobutyl ketone, or a combination thereof.
5. The process of claim 1, wherein the second solvent comprises a C1-C4 alcohol.
6. The process of claim 5, wherein the second solvent comprises methanol, ethanol, n-propanol, isopropanol, butanol, or a combination thereof.
7. The process of claim 1, wherein the heavy aromatic fraction comprises polymeric, oligomeric, and monomeric aromatic derivatives of lignin.

8. The process of claim 1, wherein the aqueous phase comprises water-soluble organic compounds and water-soluble inorganic compounds from the fast pyrolysis oil.
9. The process of claim 1, wherein combining the fast pyrolysis oil and the first solvent occurs prior to combining water or an aqueous composition with the fast pyrolysis oil.
10. The process of claim 1, wherein combining the fast pyrolysis oil and the first solvent comprises stirring or static in-line mixing.
11. The process of claim 1, wherein combining the fast pyrolysis oil and the first solvent occurs at a pressure in a range of atmospheric pressure to about 100 psig.
12. The process of claim 1, wherein heating the emulsion occurs at a temperature in a range of 15°C to 65°C.
13. The process of claim 11, wherein heating the emulsion occurs at a temperature of about 40°C.
14. The process of claim 1, wherein the liquid flow regime of the emulsion provides a Reynolds Number between 5 and 1,000,000.
15. The process of claim 1, wherein the temperature, pressure, and flow conditions of combining the fast pyrolysis oil and the first solvent and heating the emulsion are selected such that a total amount of aromatic compounds in the organic phase is at least 80% mass fraction of the total amount of aromatic compounds of the fast pyrolysis oil.
16. The process of claim 1, wherein the water comprises 15% to 35% mass fraction of the emulsion.
17. The process of claim 1, wherein the first solvent comprises 1% to 25% mass fraction of the emulsion.
18. The process of claim 1, wherein the second organic phase comprises phenolic compounds and neutral compounds.

19. The process claim 1, wherein, in the vapor stripping, a mass fraction of the second solvent to a total amount of the heavy aromatic fraction and the first solvent is in a range of 5% to 20%.
20. The process of claim 1, wherein the distilling occurs at atmospheric pressure.
21. The process of claim 1, wherein the concentrating occurs at a pressure less than atmospheric pressure.
22. The process of claim 1, wherein a total amount of carbon in the heavy aromatic fraction and the water-soluble organic fraction comprises at least 90% or at least 95% of a total amount of carbon in the fast pyrolysis oil.
23. The process of claim 1, wherein a total amount of aromatic compounds in the heavy aromatic fraction is at least 95% mass fraction of an aromatic content of the fast pyrolysis oil.
24. The process of claim 1, wherein at least 95% mass fraction of pyrolytic sugars in the fast pyrolysis oil is transferred to the water-soluble organic fraction.
25. The process of claim 1, wherein at least 80% mass fraction of inorganic compounds in the fast pyrolysis oil is transferred to the water-soluble organic fraction.
26. The process of claim 1, further comprising combining water or an aqueous composition with the emulsion to yield a second emulsion.
27. The process of claim 26, wherein combining the water or the aqueous composition with the emulsion comprises stirring or static in-line mixing.
28. The process of claim 26, wherein combining the water or the aqueous composition with the emulsion occurs at a pressure in a range of atmospheric pressure to about 100 psig.
29. The process of claim 26, wherein the liquid flow regime of the second emulsion provides a Reynolds Number between 5 and 1,000,000.

30. The process of claim 26, wherein heating the emulsion comprises heating the second emulsion, and heating the second emulsion occurs at a temperature in a range of 15°C to 65°C.
31. The process of claim 30, wherein heating the second emulsion occurs at a temperature of about 40°C.
32. The process of claim 30, wherein the temperature, pressure, and flow conditions of combining the emulsion and the water or aqueous composition and heating the second emulsion are selected such that a total amount of aromatic compounds in the organic phase is at least 80% mass fraction of the total amount of aromatic compounds of the fast pyrolysis oil.
33. The process of claim 1, further comprising:
extracting the aqueous phase with an additional amount of the first solvent to yield an additional organic phase and an aqueous raffinate; and
combining the additional organic phase with the organic phase before vapor stripping the organic phase.
34. The process of claim 33, further comprising removing water from the aqueous raffinate to yield a first stream comprising residual pyrolysis oil and a second stream comprising water.
35. The process of claim 34, wherein the second stream is a clean water stream.
36. The process of claim 34, wherein the second stream comprises water-soluble organic compounds.
37. The process of claim 36, wherein the water-soluble organic compounds comprise acetic acid, acetol, glycoaldehyde, or any combination thereof.
38. The process of claim 37, wherein the second stream comprises about 2 wt% to about 7 wt% acetic acid.

39. The process of claim 37, wherein the second stream comprises about 1 wt% to about 3 wt% acetol.
40. The process of claim 37, wherein the second stream comprises about 0.1 wt% to about 1 wt% glycolaldehyde.
41. The process of claim 34, further comprising combining the second stream with the emulsion in a recycle loop.
42. The process of claim 41, wherein combining the second stream with the emulsion occurs before heating the emulsion.
43. The process of claim 34, wherein removing water from the aqueous raffinate comprises using a multiple-effect evaporator or a membrane filtration unit.
44. A system for separating a heavy aromatic fraction from fast pyrolysis oil, the system comprising:
a mixing system comprising a feedstock inlet and configured to accept recycled downstream water and solvent;
a separator coupled to the mixing system;
a liquid-liquid extractor coupled to the separator;
a collector vessel coupled to the separator and configured to accept an input stream from the liquid-liquid extractor;
a solvent stripping column coupled to the collector vessel;
a distillation column coupled to the solvent stripping column; and
an evaporator configured to accept an aqueous raffinate from the liquid-liquid extractor, wherein the distillation column is configured to accept an overhead from the solvent stripping column and from the evaporator.
45. The system of claim 44, wherein the separator is configured to provide a heavy aromatic fraction and water-soluble organic fraction by solvent-aided emulsion inversion.

46. The system of claim 44, wherein the collector is configured to accept an aqueous raffinate from the liquid-liquid extractor.