HIGH TEMPERATURE THERMAL STABILITY ASSESSMENT OF THERMOCHEMICALLY DERIVED OILS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Patent Application No. 63/552,634 filed on February 12, 2024, and U.S. Patent Application No. 63/683,614 filed on August 15, 2024, each of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This invention relates to characterization methods suitable for differentiation of the thermal stability of thermochemically derived oils to inform the design of downstream processing conditions and for rapidly screening out oils that would be unsuitable for further processing.

BACKGROUND

[0003] The chemical complexity and oxygen content of thermochemically derived oils from oxygenated feedstocks generally prevents their use as direct replacements for transportation fuel and chemical applications. The reactive oxygenated functional groups within these molecules make it difficult to process in refineries, since they can polymerize or decompose when heated at high temperatures. Thermal degradation can occur at a range of temperatures that are dependent on the biomass or waste-derived feedstock composition, thermochemical process technology, and subsequent thermochemical oil processing steps. This is problematic for refinery unit operations such as hydrotreating that typically require temperatures above 200°C to remove oxygen, or distillation unit operations that typically require temperatures above 50°C. Thermal instability can cause fouling and plugging through the formation of coke.

SUMMARY

[0004] This disclosure describes characterization methods suitable for differentiation of the thermal stability of thermochemically derived oils to inform the design of downstream processing conditions and for rapidly screening out oils that would be unsuitable for further processing.

[0005] In a first general aspect, assessing a thermal stability of a thermochemically derived oil (e.g., "untreated" bio-oil) includes heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas, combining the treated thermochemically derived oil with a non-polar solvent to yield a mixture, and precipitating a polymeric material from the mixture.

[0006] In a second general aspect, assessing a thermal stability of a treated thermochemically derived oil includes heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas, assessing a property of the thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the thermochemically derived oil, assessing the property of the treated thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the treated thermochemically derived oil, and assessing a relative thermal stability of the treated thermochemically derived oil with respect to the thermochemically derived oil based on their respective onset temperatures for polymerization and degradation reactions.

[0007] Implementations of the first general aspect may include one or more of the following features.

[0008] The thermochemically derived oil is derived from lignocellulosic biomass or an oxygen-containing waste stream (e.g., pyrolysis oil, partially processed pyrolysis oil, aqueous fraction of pyrolysis oil, catalytic pyrolysis oil, hydrothermal liquefaction oil, partially processed hydrothermal liquefaction oil, catalytic hydrothermal liquefaction oil, or a combination thereof).

[0009] Heating the thermochemically derived oil can include heating the thermochemically derived oil to a temperature in a range of 80-400°C for a time in a range of 1 minute to four weeks. The treated thermochemically derived oil is typically cooled before combining the treated thermochemically derived oil with the non-polar solvent.

[0010] A volume ratio of the non-polar solvent to the thermochemically derived oil is typically in a range of 25:1 to 75:1 (e.g., about 50:1 to about 75:1). Suitable non-polar solvents include diethyl ether, dichloromethane, chloroform, benzene, or a combination thereof.

[0011] The precipitated polymeric material can be separated from the mixture. A mass of the polymeric material and can be assessed. A mass percent of the polymeric material relative to the mass of the thermochemically derived oil before heating (e.g., the "untreated" bio-oil) can be assessed as a measure of the stability of the thermochemically derived oil.

[0012] A suitability of the thermochemically derived oil for downstream processing can be based at least in part on the thermal stability of the thermochemically derived oil. The thermochemically derived oil can be rated for suitability for further processing based on the mass percent of the polymeric material relative to the mass of the thermochemically derived oil before heating.

[0013] Implementations of the first and second general aspects may include one or more of the following features.

[0014] The thermochemically derived oil can include pyrolysis oil, partially processed pyrolysis oil, aqueous fraction of pyrolysis oil, catalytic pyrolysis oil, hydrothermal liquefaction oil, partially processed hydrothermal liquefaction oil, catalytic hydrothermal liquefaction oil, or a combination thereof.

[0015] The heating the heating occurs for a selected length of time at a selected temperature (e.g., a temperature in a range of 80-400°C for a time in a range of 1 minute to four weeks). Heating the thermochemically derived oil includes rapidly heating the thermochemically derived oil in a reactor. Examples of suitable reactors include a sealed batch reactor and a sealed flow through reactor. The reactor typically includes the reactor a conduit to transport the thermochemically derived oil. The reactor can include one or more heater elements, optionally with one or both of temperature control and temperature monitoring. In some cases, the reactor includes a timer to measure a duration of the heating. In certain cases, the reactor includes a pump to deliver the thermochemically derived oil into a heated zone of the reactor. The reactor can include a cooling coil at the outlet of the reactor to quench the sample. The reactor can include a pressure monitoring device, an over-pressure relief valve, or both. The reactor can include a liquid sampling valve to collect the treated thermochemically derived oil, a gas sampling valve to collect decomposition gases emitted during heating of the thermochemically derived oil, or both.

[0016] Implementations of the second general aspect may include one or more of the following features.

[0017] The property may include viscosity, water content, density, molecular weight (e.g., average molecular weight), reaction pressure drop, filter pressure drop, pressure change in a headspace of the reactor, composition of the decomposition gas, or any combination thereof.

[0018] A suitability of the thermochemically derived oil for downstream processing can be based at least in part on the relative thermal stability. The thermochemically derived oil can be rated for suitability for further processing based on the relative thermal stability.

[0019] 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.

DETAILED DESCRIPTION

[0020] This disclosure describes characterization and use of thermochemically derived oils (e.g., pyrolysis oil, partially processed pyrolysis oil, aqueous fraction of pyrolysis oil, catalytic pyrolysis oil, hydrothermal liquefaction oil, partially processed hydrothermal liquefaction oil, catalytic hydrothermal liquefaction oil, etc.) derived from lignocellulosic biomass and oxygen-containing waste streams. In this disclosure, "bio-oil" is used interchangeably with "thermochemically derived oil." The characterization methods are suitable for differentiation of the thermal stability of thermochemically derived oils to inform the design of downstream processing conditions and for rapidly screening out oils that would be unsuitable for further processing.

[0021] In some implementations, assessing a thermal stability of a thermochemically derived oil (e.g., a "starting" or "untreated" bio-oil) includes heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas, assessing a property of the thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the thermochemically derived oil, assessing the property of the treated thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the treated thermochemically derived oil, and assessing a relative thermal stability of the treated thermochemically derived oil with respect to the thermochemically derived oil based on their respective onset temperatures for polymerization and degradation reactions.

[0022] In some implementations, assessing a thermal stability of a thermochemically derived oil (e.g., a "starting" or "untreated" bio-oil) includes heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas, combining the treated thermochemically derived oil with a non-polar solvent to yield a mixture, and precipitating a

polymeric material from the mixture. The precipitated polymeric material is separated from the mixture. Combining the treated thermochemically derived oil with the non-polar solvent and precipitating the polymer material can be referred to as fractionating the treated thermochemically derived oil to yield a fractionated (or solvent fractionated) oil. A mass of the polymeric material is assessed. A mass percent of the polymeric material relative to the mass of the thermochemically derived oil (the "starting" or "untreated" bio-oil) is assessed as a measure of the stability of the thermochemically derived oil.

[0023] Examples of suitable thermochemically derived oils include pyrolysis oil, partially processed pyrolysis oil, aqueous fraction of pyrolysis oil, catalytic pyrolysis oil, hydrothermal liquefaction oil, partially processed hydrothermal liquefaction oil, catalytic hydrothermal liquefaction oil, or a combination thereof.

[0024] Heating the thermochemically derived oil can include rapidly heating the thermochemically derived oil in a reactor, thereby thermally stressing the thermochemically derived oil to yield the treated thermochemically derived oil.

[0025] Examples of suitable reactors include a sealed batch reactor or a sealed flow through reactor. The reactor can include one or more of the following components in one or more combinations: a heater element with temperature control and temperature monitoring; a timer to measure a duration of the heating; a pump to deliver the thermochemically derived oil into a heated zone of the reactor; a conduit to transport the thermochemically derived oil; a cooling coil at the outlet of the reactor to quench the sample; a pressure monitoring device; an over-pressure relief valve; a liquid sampling valve to collect oil; a gas sampling valve to collect decomposition gases emitted during heating of the thermochemically derived oil.

[0026] The property of the thermochemically derived oil and treated thermochemically derived oil can include one or more of the following in any combination: viscosity, water content, density, molecular weight, reaction pressure drop in the reactor, filter pressure drop in the reactor, pressure change in a headspace of the reactor, composition of the decomposition gas.

[0027] The heating can occur for a selected length of time at a selected temperature or a combination of selected times and selected temperatures. In some cases, the heating can be selected to deliver a selected amount of heat (e.g., total heat exposure) to the thermochemically derived oil.

[0028] A suitability of the thermochemically derived oil for downstream processing can be determined based at least in part on the relative thermal stability (e.g., heating for a selected length of time at a selected temperature or heating to achieve a total heat exposure). The thermochemically derived oil can be rated for suitability for further processing based on the relative thermal stability.

[0029] In some examples, untreated bio-oil is thermally treated by heating the bio-oil in a reactor to an elevated temperature for a length of time. The untreated bio-oil can be placed in a stirred batch reactor vessel, followed by purging of the headspace with inert gas. Depending on the intended application and the composition of the untreated bio-oil, heat treatment conditions can range from 80-400°C at 1 minute to multiple weeks (e.g., four weeks). Bio-oil storage stability can be evaluated with lower heat and longer hold times, while refinery applications can be evaluated at higher temperatures and shorter hold times. The treated bio-oil is cooled (e.g., to room temperature, or 20-25°C).

[0030] The extent of polymerization of components in the untreated bio-oil can be assessed by precipitation and separation of polymeric material formed during heating of the untreated bio-oil. The mass percent polymeric material formed during the heating can be used to rank the relative thermal stability of the bio-oil. To assess the amount of polymeric material formed during heating, the treated bio-oil is combined with an excess amount of a non-polar solvent to separate the polymeric material from the bio-oil. Examples of suitable non-polar solvents include diethyl ether, dichloromethane, chloroform, benzene, or a combination thereof. A volume ratio of solvent to heat treated bio-oil is typically in a range of about 25:1 to about 75:1 (e.g., about 50:1). Combining the treated bio-oil and the solvent can be performed in a variety of vessels. The polymeric material is then isolated via precipitation in the non-polar solvent. After precipitation, the polymeric material is separated from the treated bio-oil (e.g., by filtering), and the mass of polymeric material is assessed to determine the mass percent of polymeric material in the treated bio-oil. The relative stability of the treated bio-oil is based at least in part on the mass percent of polymeric material (i.e., a ratio of the mass of the polymeric material to the mass of the untreated bio-oil). Ranking is based on a value of 0 to 100%, with a lower value signifying higher relative thermal stability. Solvent fractionated bio-oils with high thermal stability typically yield polymeric material of 15 mass % to 20 mass %, while non-fractionated fast pyrolysis bio-oil displays poor thermal stability yielding polymeric material of > 55 mass %.

EXAMPLES

[0031] The thermal stability of fast pyrolysis bio-oil produced from woody biomass from two commercial fast pyrolysis technologies, as well as bio-oils produced from energy grass biomass were assessed as follows: 60 mL of each bio-oil sample was thermally treated by heating in a stirred batch reactor vessel, purging the headspace with inert gas, and heating the bio-oil to 300°C for 1 hour. Heat treatment without stirring was also applied and shown to be equivalent. The bio-oil was then cooled to room temperature, and the treated bio-oil was then recovered. To analyze the amount of polymeric material formed during heat treatment, 0.5 mL of the treated bio-oil was combined with 25 mL of diethyl ether to yield a mixture. The mixture was homogenized and via vortex mixing and allowed to settle at ambient temperature for 5 to 10 minutes, then filtered with a glass fiber filter (1.0 μm pore size) to capture the precipitated polymeric material. The filter was dried at 95 to 105 °C to remove residual solvent and moisture. The filter with the polymeric material was cooled inside a desiccator. The polymeric material on the filter was weighed to determine the mass of the precipitated polymeric material, and the mass percent of the precipitated polymeric material relative to the treated bio-oil was calculated. Test results, including a control (bio-oil before heat treatment) are shown in Table 1.

Table 1. Thermal stability testing of non-fractionated fast pyrolysis oil and solvent fractionated fast pyrolysis oil derived from lignocellulosic biomass.

Non-fractionated and solvent fractionated fast pyrolysis oil	**Mass % of polymeric material**
Sample 1: Solvent fractionated bio-oil before heat treatment	2.5 ± 0.2
Sample 2: High thermal stability solvent fractionated bio-oil	16.1 ± 0.2
Sample 3: Low thermal stability solvent fractionated bio-oil	33.2 ± 3.2
Sample 4: Non-fractionated bio-oil with 15 wt. % ethanol	57.9 ± 0.7

[0032] 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.

[0033] 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.

[0034] 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 method of assessing a thermal stability of a thermochemically derived oil, the method comprising:

heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas;

combining the treated thermochemically derived oil with a non-polar solvent to yield a mixture; and

precipitating a polymeric material from the mixture to yield a precipitated polymeric material.

2. The method of claim 1, wherein heating the thermochemically derived oil comprises heating the thermochemically derived oil to a temperature in a range of 80-400°C for a time in a range of 1 minute to four weeks.

3. The method of claim 1, further comprising cooling the treated thermochemically derived oil before combining the treated thermochemically derived oil with the non-polar solvent.

4. The method of claim 1, further comprising separating the precipitated polymeric material from the mixture.

5. The method of claim 4, further comprising assessing a mass of the polymeric material.

6. The method of claim 5, further comprising assessing a mass percent of the polymeric material relative to the mass of the thermochemically derived oil before heating.

7. The method of claim 6, further comprising assessing a suitability of the thermochemically derived oil for downstream processing based at least in part on the mass percent of the polymeric material relative to the mass of the thermochemically derived oil before heating.

8. The method of claim 6, further comprising rating the thermochemically derived oil for suitability for further processing based at least in part on the mass percent of the polymeric material relative to the mass of the thermochemically derived oil before heating.

9. The method of claim 1, wherein a volume ratio of the non-polar solvent to the thermochemically derived oil is in a range of 25:1 to 75:1.

10. The method of claim 9, wherein the volume ratio of the non-polar solvent to the thermochemically derived oil is in a range of 50:1 to 75:1.

11. The method of claim 1, wherein the non-polar solvent comprises diethyl ether, dichloromethane, chloroform, benzene, or a combination thereof.

12. The method of claim 1, wherein the thermochemically derived oil is derived from lignocellulosic biomass or an oxygen-containing waste stream.

13. The method of claim 1, wherein the thermochemically derived oil comprises pyrolysis oil, partially processed pyrolysis oil, aqueous fraction of pyrolysis oil, catalytic pyrolysis oil, hydrothermal liquefaction oil, partially processed hydrothermal liquefaction oil, catalytic hydrothermal liquefaction oil, or a combination thereof.

14. The method of claim 1, wherein heating the thermochemically derived oil comprises rapidly heating the thermochemically derived oil in a reactor.

15. The method of claim 14, wherein the reactor comprises a sealed batch reactor or a sealed flow through reactor.

16. The method of claim 14, wherein the reactor comprises a heater element with temperature control and temperature monitoring.

17. The method of claim 14, wherein the reactor comprises a timer to measure a duration of the heating.

18. The method of claim 14, wherein the reactor comprises a pump to deliver the thermochemically derived oil into a heated zone of the reactor.

19. The method of claim 14, wherein the reactor comprises a conduit to transport the thermochemically derived oil.

20. The method of claim 14, wherein the reactor comprises a cooling coil at the outlet of the reactor to quench the treated thermochemically derived oil.

21. The method of claim 14, wherein the reactor comprises a pressure monitoring device.

22. The method of claim 14, wherein the reactor comprises an over-pressure relief valve.

23. The method of claim 14, wherein the reactor comprises a liquid sampling valve to collect the treated thermochemically derived oil.

24. The method of claim 14, wherein the reactor comprises a gas sampling valve to collect decomposition gases emitted during heating of the thermochemically derived oil.

25. A method of assessing a thermal stability of a treated thermochemically derived oil, the method comprising:

heating the thermochemically derived oil to yield a treated thermochemically derived oil and a decomposition gas;

assessing a property of the thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the thermochemically derived oil;

assessing the property of the treated thermochemically derived oil based on an onset temperature for polymerization and degradation reactions of the treated thermochemically derived oil; and

assessing a relative thermal stability of the treated thermochemically derived oil with respect to the thermochemically derived oil based on their respective onset temperatures for polymerization and degradation reactions.

26. The method of claim 25, wherein the property comprises viscosity.

27. The method of claim 25, wherein the property comprises water content.

28. The method of claim 25, wherein the property comprises density.

29. The method of claim 25, wherein the property comprises molecular weight.

30. The method of claim 25, wherein the property comprises reaction pressure drop.

31. The method of claim 25, wherein the property comprises filter pressure drop.

32. The method of claim 25, wherein the property comprises pressure change in a headspace of the reactor.

33. The method of claim 25, wherein the property comprises composition of the decomposition gas.

34. The method of claim 25, further comprising assessing a suitability of the thermochemically derived oil for downstream processing based at least in part on the relative thermal stability.

35. The method of claim , further comprising rating the thermochemically derived oil for suitability for further processing based on the relative thermal stability.