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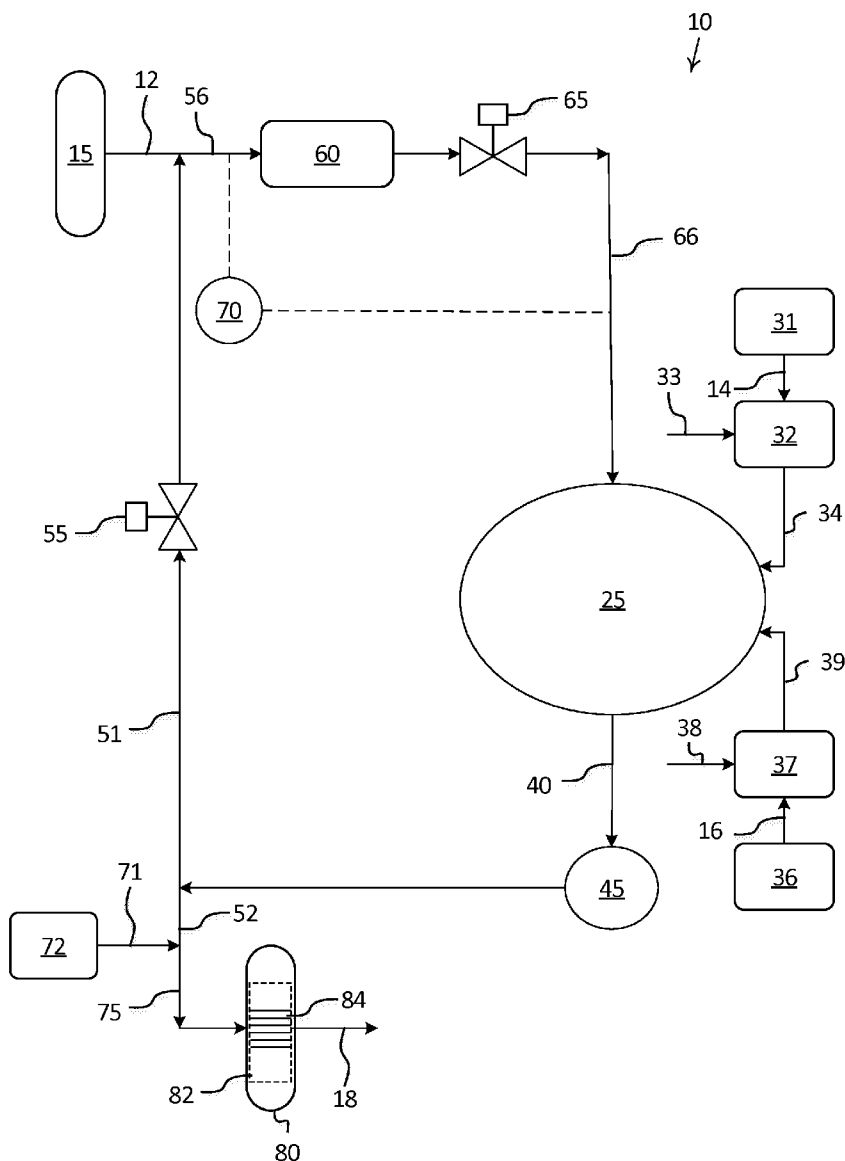
(57) **ABSTRACT**

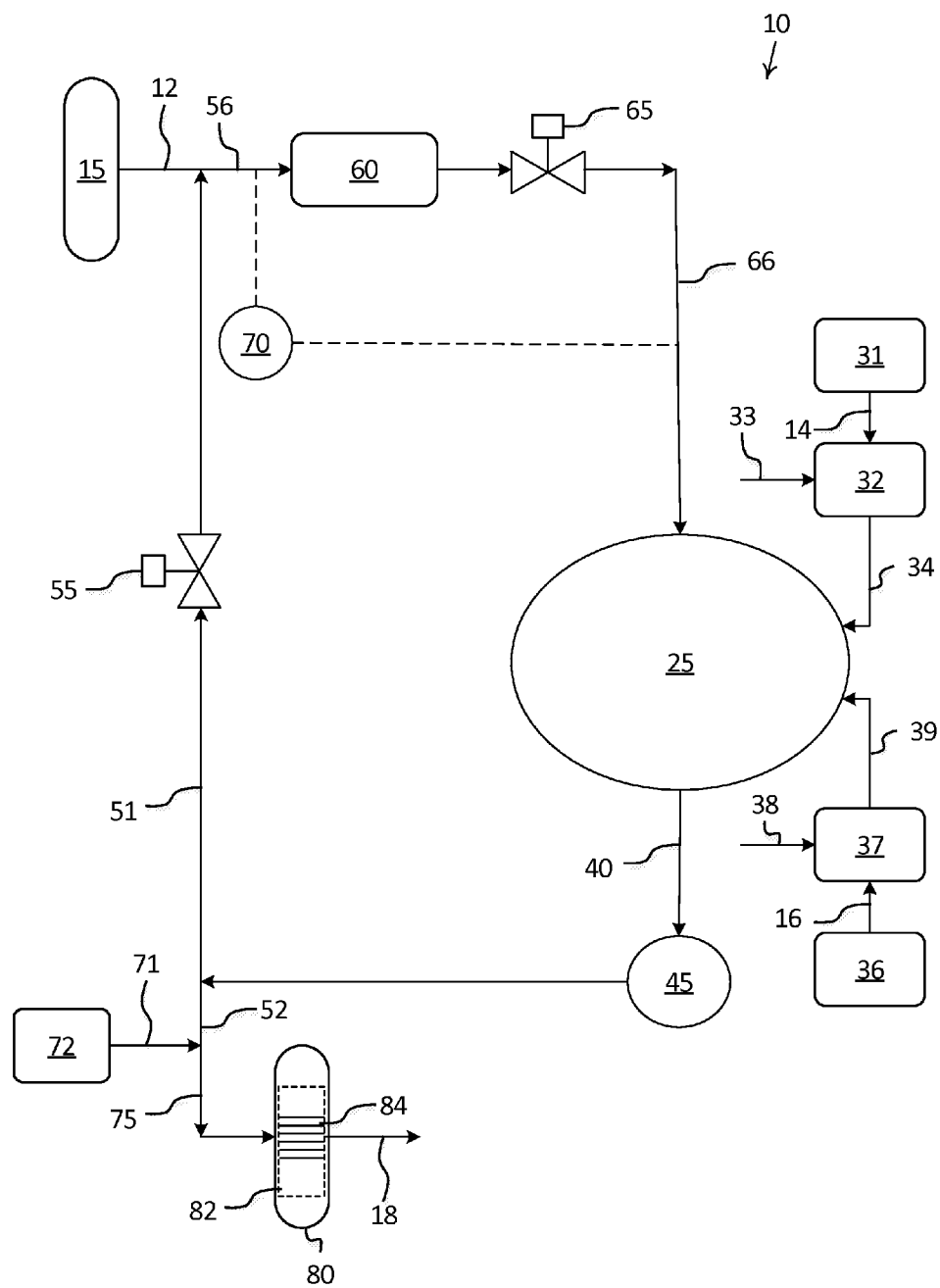
Methods for co-processing pyrolysis oil streams and fuel processing apparatuses are provided. In one example, a method for co-processing a pyrolysis oil stream and a hydrocarbon stream is provided. The method includes mixing the pyrolysis oil stream and the hydrocarbon stream with a surfactant to form an emulsion. The method introduces the emulsion to a reaction zone in an fluid catalytic cracking (FCC) unit. The method includes contacting the emulsion with a catalyst in the reaction zone to form an FCC product stream.

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FIGURE

METHODS AND APPARATUSES FOR CO-PROCESSING PYROLYSIS OIL

TECHNICAL FIELD

[0001] The technical field generally relates to methods and apparatuses for co-processing pyrolysis oil. More particularly, the technical field relates to methods and apparatuses for co-processing pyrolysis oil with another feedstock stream in a Fluid Catalyst Cracking (FCC) unit to form an FCC product stream containing renewable components.

BACKGROUND

[0002] As the demand for fuel increases worldwide there is increasing interest in sources other than petroleum crude oil for producing fuel. Specifically, biological sources are being investigated for use in supplementing or replacing petroleum crude oil as the primary feedstock in hydrocarbon processing. Bio-derived sources include biomass, such as plant oils including corn, rapeseed, canola, soybean and algal oils; animal fats such as tallow, fish oils and various waste streams such as yellow and brown greases; and sewage sludge. Bio-derived sources also include carbon-based products formed by engineered organisms, such as engineered algae cells.

[0003] Lignocellulosic biomass is particularly suited for processing into pyrolysis oil. Such biomass may be converted to pyrolysis oil by rapid thermal processing or by pyrolysis technologies such as a bubble-column, auger or intermediate pyrolysis systems. Because lignocellulosic biomass is much more abundant than vegetable oils, pyrolysis oil is less expensive. However, pyrolysis oil has a much higher oxygen content (about 45%) compared to vegetable oil feedstocks (about 11%). Further, it may contain up to about 35% water and also contain acidic components that may cause corrosion.

[0004] The high water content and acidic content of pyrolysis oil makes processing in FCC units challenging. Specifically, the high volume of water in a pyrolysis stream introduced to an FCC unit negatively impacts the heat balance of the FCC unit. Further, the acid content of the pyrolysis stream can potentially harm FCC catalysts, such as through accelerated coke formation, and reduce the FCC unit product yield.

[0005] Accordingly, it is desirable to provide methods and apparatuses for processing pyrolysis oil in an FCC unit. Also, it is desirable to provide methods and apparatuses for co-processing pyrolysis oil in an FCC unit. Further, it is desirable to provide methods and apparatuses for increasing the renewable content of FCC product streams. Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.

BRIEF SUMMARY

[0006] Methods for co-processing pyrolysis oil streams and fuel processing apparatuses are provided. In an embodiment, a method for co-processing a pyrolysis oil stream and a hydrocarbon stream is provided. The method includes mixing the pyrolysis oil stream and the hydrocarbon stream with a surfactant to form an emulsion. The method introduces the emulsion to a reaction zone in an fluid catalytic cracking (FCC) unit. The method includes contacting the emulsion with a catalyst in the reaction zone to form an FCC product stream.

[0007] In another embodiment, a method for co-processing a pyrolysis oil stream and a lipid stream are provided. The method includes mixing the pyrolysis oil stream and the lipid stream with a surfactant to form a mixture. The method introduces the mixture to a reaction zone in an fluid catalytic cracking (FCC) unit. Further, the method includes contacting the mixture with a catalyst in the reaction zone to form an FCC product stream.

[0008] In another embodiment, a fuel processing apparatus is provided. The fuel processing apparatus includes a pyrolysis oil source and a mixing unit in fluid communication with the pyrolysis oil source and configured to mix pyrolysis oil, a hydrocarbon feedstock, and a surfactant to form an emulsion. The fuel processing apparatus also includes a fluid catalytic cracking (FCC) unit in fluid communication with the mixing unit and including a reaction chamber suitable for contacting components of the emulsion with a catalyst to form an FCC product stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The various embodiments will hereinafter be described in conjunction with the following drawing FIGURE, wherein:

[0010] The FIGURE is a schematic diagram of an apparatus and a method for co-processing a pyrolysis oil stream in accordance with an exemplary embodiment.

DETAILED DESCRIPTION

[0011] The following Detailed Description is merely exemplary in nature and is not intended to limit the methods and apparatuses described herein. Furthermore, there is no intention to be bound by any theory presented in the preceding Background or the following detailed description.

[0012] Various embodiments contemplated herein relate to methods and apparatuses for co-processing pyrolysis oil. Specifically, embodiments herein provide for co-processing pyrolysis oil in an FCC reactor with another stream, such as a hydrocarbon stream and/or a lipid stream. An exemplary process uses a surfactant to form an emulsion from the pyrolysis oil, the hydrocarbon stream, and the surfactant. The emulsion is fed directly into the FCC reactor through conventional means, i.e., no special injection equipment is needed. The FCC reactor converts the emulsion into an FCC product stream including upgraded fuel products. The FCC product stream may be distilled into various streams including naphtha, light coker oil, and decant oil.

[0013] The FIGURE illustrates an exemplary apparatus 10 utilizing an exemplary method for co-processing a pyrolysis oil stream 12 with a hydrocarbon stream 14 and/or a lipid stream 16 to form an FCC product stream 18. In the illustrated embodiment, the pyrolysis oil stream 12 is provided by a pyrolysis oil source 15. For example, the pyrolysis oil source 15 may be a pyrolysis reactor for converting biomass into pyrolysis oil.

[0014] Pyrolysis is the thermal decomposition of a substance into its elemental components and/or smaller molecules. Pyrolysis typically requires temperatures of about 325° C. or higher to sufficiently decompose the feedstock to produce pyrolysis products. Pyrolysis of a biomass feedstock typically produces water, pyrolysis oil or bio-oil, char, and gases such as hydrogen, carbon monoxide, carbon dioxide, methane and other light hydrocarbons that do not condense under typical conditions,

[0015] Pyrolysis of lignocellulosic biomass typically produces organic compounds such as lignin fragments, aldehydes, carboxylic acids, phenols, furfurals, alcohols, and ketones, as well as water. The exemplary pyrolysis oil stream 12 is provided to apparatus 10 as a full, non-fractionated pyrolysis reaction product. For example, the pyrolysis oil stream 12 may include from about 15 volume percent (vol %) water to about 35 vol % water.

[0016] In the FIGURE, the pyrolysis oil stream 12 is fed into a tank or settler 25. Further, the tank 25 receives the hydrocarbon stream 14 and/or lipid stream 16. An exemplary hydrocarbon stream 14 may be any appropriate petroleum-based fraction. In an embodiment the hydrocarbon stream 14 is a diesel stream or an atmospheric gas oil stream. The hydrocarbon stream 14 is provided by a hydrocarbon source 31, such as a processing unit located elsewhere in the apparatus 10. In the exemplary embodiment, the hydrocarbon stream 14 is fed to a tank or drum 32. As shown, drum 32 also receives a surfactant 33. In an exemplary embodiment, the surfactant is dissolved in the hydrocarbon stream 14 in drum 32. Drum 32 may be provided with a mixing apparatus to facilitate dissolution.

[0017] An exemplary lipid stream 16 may be any suitable lipid stream including vegetable oils, animal fats, algal oils, used cooking oil, triglycerides, esters, fatty acids, or mixtures thereof. The lipid stream 16 is provided by a lipid source 36, such as a processing unit located elsewhere in the apparatus 10. In the exemplary embodiment, lipid stream 16 is fed to a tank or drum 37. As shown, drum 37 also receives a surfactant 38. In an exemplary embodiment, the surfactant 38 is dissolved in the lipid stream 16 in drum 37. Drum 37 may be provided with a mixing apparatus to facilitate dissolution.

[0018] In an exemplary embodiment, each surfactant 33 and 38 is a non-ionic surfactant. Surfactant 33 may be the same as or different from surfactant 38. For example, the surfactant 33 and/or 38 may be or include sorbitan esters of fatty acids, polyglycol esters of fatty acids, mono-glycerides, di-glycerides, a mixture of mono-glycerides and di-glycerides, esters of monofunctional fatty acids with poly-12-hydroxystearic acid, esters of monofunctional alcohols with poly-12-hydroxystearic acid, polymeric esters of difunctional fatty acids, polymeric esters of difunctional alcohols, esters of fatty acids with polyethylene glycol having up to five polyoxyethylene units, esters of hydroxyacids with polyethylene glycol having up to five polyoxyethylene units, succinic anhydride or succinimide-modified linear and branched polyalkylene compounds. Blends of two or more surfactants can be used. In some cases, blends may provide better results than a single surfactant, or else may permit the use of a smaller total amount of surfactant.

[0019] A stream 34 of hydrocarbon with dissolved surfactant and/or a stream 39 of lipids with dissolved surfactant is fed to the tank 25. An exemplary tank 25 is provided with a motor driven multi-bed agitator. As a result of the agitation, an effluent 40 is formed.

[0020] When the hydrocarbon stream 14 is fed to the tank 25, the effluent 40 may be formed as an emulsion and a dispersed phase. In an exemplary embodiment, the stream 34 and pyrolysis oil stream 12 are fed in proportion to one another to form the effluent 40 with a content of from about 1 to about 55 vol % pyrolysis oil stream, from about 45 to about 50 vol % hydrocarbon stream, and about 0.5 to about 5 vol % surfactant. In another embodiment, the effluent 40 may be formed with a content of from about 1 to about 8 vol %

pyrolysis oil stream, from about 87 to about 99 vol % hydrocarbon stream, and about 0.5 to about 5 vol % surfactant. In other embodiments, the effluent 40 may be formed with a content of from about 48 to about 52 vol % pyrolysis oil stream, from about 47 to about 48 vol % hydrocarbon stream, and from about 2 to about 3 vol % surfactant.

[0021] In cases in which the pyrolysis oil stream 12, lipids stream 16, and surfactant 38 are mixed, without hydrocarbon stream 14 and surfactant 33, the effluent 40 may be a single phase, stable mixture of the lipids and the pyrolysis oil.

[0022] In an exemplary embodiment, the stream 39 and pyrolysis oil stream 12 are fed in proportion to one another to form the effluent 40 with a content of from about 1 to about 55 vol % pyrolysis oil stream 12, from about 45 to about 50 vol % lipid stream 16, and about 0.5 to about 5 vol % surfactant 38. In another embodiment, the effluent 40 may be formed with a content of from about 1 to about 8 vol % pyrolysis oil stream 12, from about 87 to about 99 vol % lipid stream 16, and about 0.5 to about 5 vol % surfactant 38. In other embodiments, the effluent 40 may be formed with a content of from about 48 to about 52 vol % pyrolysis oil stream 12, from about 47 to about 48 vol % lipid stream 16, and from about 2 to about 3 vol % surfactant 38.

[0023] In certain embodiments, the pyrolysis oil stream 12 is included in amounts up to about 50 vol % of the lipid stream 16, such as up to about 40 vol %, up to about 30 vol %, or up to about 20 vol %, of the lipid stream. Exemplary embodiments include at least about 1 vol % pyrolysis oil in the effluent 40, such as at least about 3 vol %, or at least about 5 vol % pyrolysis oil in the effluent 40.

[0024] The exemplary effluent 40 includes an effective amount of non-ionic surfactant 38, which compatibilizes the lipids and the pyrolysis oil, and allows the formation of a single phase, stable mixture of the two materials. The selection of the non-ionic surfactant 38 can be optimized for the particular lipid feedstock being used. The amount of non-ionic surfactant 38 may vary depending on the particular lipid feedstock and pyrolysis oil being used, and the ratio of these two components in the effluent 40.

[0025] An effective amount of surfactant 38 is any amount equal to or above the minimum amount that results in the formation of a single phase, stable mixture. There is no upper limit to the amount of surfactant 38 that can be used. However, above a certain level, the use of more surfactant 38 does not result in the enhancement of the stability of the mixture. Although it is possible to use more than this amount without having a negative physical effect on the composition, the cost of the composition would increase. Consequently, using more surfactant than needed to provide the stability benefit is less desirable.

[0026] In general, the greater the amount of pyrolysis oil in the composition, the greater the amount of non-ionic surfactant used in the composition. The amount of non-ionic surfactant used is typically at least about 0.2% by weight of pyrolysis oil in the composition, although some surfactants may require at least about 0.3%, or at least about 0.4%, or at least about 0.5%, or at least about 0.6%. Typically, the maximum amount of surfactant that enhances the stability of the mixture is about 1% by weight of pyrolysis oil in the composition. The amount of surfactant that might be used in practice, depending on the conditions of storage, handling and desired shelf life of the composition, is typically less than

about 10% by weight of pyrolysis oil in the composition, or less than about 5%, or less than about 3%, or less than about 2%, or less than about 1%.

[0027] The effluent 40 can also include one or more lower alcohols or polyols with carbon numbers of 3 to 8, such as butanol, propylene glycol and the like, for increased stability, if desired. The exemplary effluent 40 is a stable, intimate mixture of the lipid stream 16 and the pyrolysis oil stream 12.

[0028] The hydrocarbon stream 14, surfactant 33, lipid stream 16 and/or surfactant 38 may be heated. If any component is a solid or paste at ambient temperature, it is heated to a temperature at which it is a liquid. If either the lipid stream 16 or the surfactant 38 is heated before being mixed, the other should be heated to a temperature within about 5 degrees of the same temperature. Similarly, if either the hydrocarbon 14 stream or the surfactant 33 is heated before being mixed, the other should be heated to a temperature within about 5 degrees of the same temperature.

[0029] Mixing of the surfactant 33 or 38 and the hydrocarbon stream 14 or lipid stream 16 may be performed in a series of mixing tanks. For example, an appropriate amount of one or more surfactants (generally in the range of about 0.2 to about 1% by weight of pyrolysis oil to be included) may be fed slowly into the lipid stream 16. To the extent possible, laminar flow mixing should be maintained. After all of the surfactant has been mixed in, mixing may be continued for a period of time to ensure thorough mixing of the surfactant 38 in the lipid stream 16. The additional mixing period can be about 15 min to about 2 hours or more.

[0030] Then, the pyrolysis oil stream 14 may be slowly added to the lipid/surfactant mixture 39 in the tank 25 while maintaining mixing and heating (if any). After the addition of the pyrolysis oil has been completed, any heating is turned off, and mixing is continued for a period of time, such as about 15 min to about 2 hours or more.

[0031] The effluent 40 can be filtered to remove any coarse particles that may be present, if desired. The effluent 40 can then be used in processes designed for pure lipid feedstocks, or pure hydrocarbon feedstocks, without any additional upgrading of the pyrolysis oil or any significant modifications to the process equipment.

[0032] As shown, the effluent 40 is pumped by a circulation pump 45. A recycle portion 51 is redirected for mixing with the pyrolysis oil stream 12 while a product portion 52 flows into product processing. As shown, the recycle portion 51 passes through a flow control valve 55 for maintaining an appropriate ratio of recycle effluent 40 and fresh pyrolysis oil stream 12. The recycle portion 51 is then introduced to the pyrolysis oil stream 12 to form a combined stream 56. The combined stream 56 is mixed together. Specifically, the combined stream 56 passes through a static mixer 60 and through a mixing valve 65 to form mixed stream 66. Mixed stream 66 is fed to the tank 25. In this manner, the pyrolysis oil stream 12 is introduced to the tank 25.

[0033] As shown, the apparatus 10 may include a pressure differential indicator controller (PDIC) 70 connected to the pyrolysis oil stream 12 and the combined stream 56. The controller 70 is utilized to ensure a fixed pressure drop from combined stream 56 to mixed stream 66 through mixing valve 65 to ensure proper mixing of the pyrolysis oil stream 12 and the recycle portion 51 before introduction to the tank 25.

[0034] The product portion 52 of the effluent 40 may be optionally blended with a hydrocarbon stream 71 from a hydrocarbon source 72 to form a blended stream 75. In an

exemplary embodiment, the hydrocarbon source 72 is a processing unit from elsewhere in apparatus 10. While any suitable and available hydrocarbon stream may be blended, an exemplary hydrocarbon stream 71 is a vacuum gas oil (VGO) stream.

[0035] The product portion 52 of the effluent 40, optionally in the form of blended stream 75, is fed to and processed by an FCC reactor 80. As shown, the FCC reactor 80 includes a reaction zone 82 holding catalyst 84. The effluent 40 or blended stream 75 is fed into the FCC reactor 80 through a main feed line. In other words, the effluent 40 or blended stream 75 need not be introduced into the FCC reactor 80 through special injectors or nozzles. Further, the components of the pyrolysis oil stream 12, hydrocarbon stream 14, lipid stream 16, surfactant stream 33, surfactant stream 38, and/or hydrocarbon stream 70 are introduced to the FCC reactor 80 in a single stream, rather than separately.

[0036] Accordingly, methods and apparatuses for co-processing pyrolysis oil streams have been described. The various embodiments comprise upgrading a pyrolysis oil through mixing with a hydrocarbon stream and surfactant and/or with a lipid stream and surfactant. Further, the embodiments provide for FCC processing of the effluent formed by mixing the pyrolysis oil and the selected stream or streams without requiring water removal.

[0037] While at least one exemplary embodiment has been presented in the foregoing detailed description, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the subject matter. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope as set forth in the appended claims.

What is claimed is:

1. A method for co-processing a pyrolysis oil stream and a hydrocarbon stream, the method comprising the steps of:

mixing the pyrolysis oil stream and the hydrocarbon stream with a surfactant to form an emulsion;
introducing the emulsion to a reaction zone in an fluid catalytic cracking (FCC) unit; and
contacting the emulsion with a catalyst in the reaction zone to form an FCC product stream.

2. The method of claim 1 wherein the pyrolysis oil stream comprises from about 15 vol % water to about 35 vol % water.

3. The method of claim 1 further comprising dissolving the surfactant in the hydrocarbon stream before mixing the pyrolysis oil stream and the hydrocarbon stream.

4. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion comprises mixing the pyrolysis oil stream and the hydrocarbon stream with a non-ionic surfactant.

5. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion comprises mixing the pyrolysis oil stream and the hydrocarbon stream with sorbitan esters of fatty acids, polyglycol esters of fatty acids, mono-glycerides, di-glycerides, a mixture of mono-glycerides and di-glycerides, esters of monofunctional fatty acids with poly-12-hydroxystearic acid, esters of monofunctional alcohols with poly-12-hydrox-

ystearic acid, polymeric esters of difunctional fatty acids, polymeric esters of difunctional alcohols, esters of fatty acids with polyethylene glycol having up to five polyoxyethylene units, esters of hydroxyacids with polyethylene glycol having up to five polyoxyethylene units, succinic anhydride or succinimide-modified linear and branched polyalkylene compounds, or mixtures thereof.

6. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion comprises forming the emulsion with a content of from about 1 to about 55 vol % pyrolysis oil stream, from about 45 to about 50 vol % hydrocarbon stream, and about 0.5 to about 5 vol % surfactant.

7. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion comprises forming the emulsion with a content of from about 1 to about 8 vol % pyrolysis oil stream, from about 87 to about 99 vol % hydrocarbon stream, and about 0.5 to about 5 vol % surfactant.

8. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion comprises forming the emulsion with a content of from about 48 to about 52 vol % pyrolysis oil stream, from about 47 to about 48 vol % hydrocarbon stream, and about 2 to about 3 vol % surfactant.

9. The method of claim 1 wherein:

the hydrocarbon stream is a diesel stream or an atmospheric gas oil stream;

mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant comprises mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion;

the method further comprises blending the emulsion with a vacuum gas oil (VGO) stream to form a blended stream; introducing the emulsion to the reaction zone in the FCC unit comprises introducing the blended stream to the reaction zone in the FCC unit; and

contacting the emulsion with the catalyst in the reaction zone comprises contacting the blended stream with the catalyst in the reaction zone to form the FCC product stream.

10. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant comprises mixing the pyrolysis oil stream, the hydrocarbon stream and a lipid stream with the surfactant to form the emulsion.

11. The method of claim 1 wherein mixing the pyrolysis oil stream and the hydrocarbon stream with the surfactant to form the emulsion further comprises forming a dispersed phase.

12. A method for co-processing a pyrolysis oil stream and a lipid stream, the method comprising the steps of:

mixing the pyrolysis oil stream and the lipid stream with a surfactant to form a mixture;

introducing the mixture to a reaction zone in a fluid catalytic cracking (FCC) unit; and contacting the mixture with a catalyst in the reaction zone to form an FCC product stream.

13. The method of claim 12 wherein the pyrolysis oil stream comprises from about 15 vol % water to about 35 vol % water.

14. The method of claim 12 further comprising dissolving the surfactant in the lipid stream before mixing the pyrolysis oil stream and the lipid stream.

15. The method of claim 12 wherein mixing the pyrolysis oil stream and the lipid stream with the surfactant comprises mixing the pyrolysis oil stream and the lipid stream with a non-ionic surfactant.

16. The method of claim 12 wherein mixing the pyrolysis oil stream and the lipid stream with the surfactant comprises mixing the pyrolysis oil stream and the lipid stream with sorbitan esters of fatty acids, polyglycol esters of fatty acids, mono-glycerides, di-glycerides, a mixture of mono-glycerides and di-glycerides, esters of monofunctional fatty acids with poly-12-hydroxystearic acid, esters of monofunctional alcohols with poly-12-hydroxystearic acid, polymeric esters of difunctional fatty acids, polymeric esters of difunctional alcohols, esters of fatty acids with polyethylene glycol having up to five polyoxyethylene units, esters of hydroxyacids with polyethylene glycol having up to five polyoxyethylene units, succinic anhydride or succinimide-modified linear and branched polyalkylene compounds, or mixtures thereof.

17. The method of claim 12 wherein mixing the pyrolysis oil stream and the lipid stream with the surfactant to form the mixture comprises forming the mixture with a content of from about 1 to about 55 vol % pyrolysis oil stream, from about 45 to about 50 vol % lipid stream, and about 0.5 to about 5 vol % surfactant.

18. The method of claim 12 wherein mixing the pyrolysis oil stream and the lipid stream with the surfactant to form the mixture comprises forming the mixture with a content of from about 1 to about 8 vol % pyrolysis oil stream, from about 87 to about 99 vol % lipid stream, and about 0.5 to about 5 vol % surfactant.

19. A fuel processing apparatus comprising:

a pyrolysis oil source;

a mixing unit in fluid communication with the pyrolysis oil source and configured to mix a pyrolysis oil, a hydrocarbon feedstock, and a surfactant to form an emulsion; and

a fluid catalytic cracking (FCC) unit in fluid communication with the mixing unit and including a reaction chamber suitable for contacting components of the emulsion with a catalyst to form an FCC product stream.

20. The fuel processing apparatus of claim 19 wherein the apparatus is configured to blend the emulsion with a gas oil stream to form a blended stream, wherein the blended stream is fed to the FCC unit.

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