

WATER-WASHED RECYCLE PYROLYSIS OIL FOR CRACKER FEED**FIELD**

[0001] This application relates to cracking hydrocarbons and, more particularly, in one or more embodiments, relates to methods and systems that include water washing of a recycle
5 pyrolysis oil for feed to a cracker.

BACKGROUND

[0002] The rate of plastic production has steadily increased in the past century to a global value of about 400 million tons (MT) in 2016 with a corresponding increase in plastic waste. Several waste-valorization methods have been proposed over the years ranging from direct
10 recycling to energy generation from plastic waste. One pathway for recycling of plastic waste is to combine plastic waste with conventional petroleum feedstocks for co-processing in conventional refinery processes, such as thermal conversion processes (e.g., coking, visbreaking, or other pyrolysis) and/or catalytic conversion processes (such as fluid catalytic cracking). In one example, a pyrolysis process can be used to convert plastic waste into an oil
15 (e.g., recycle pyrolysis oil) through thermal degradation of the polymers contained in the plastic waste. Recycle pyrolysis oil (and other recycle pyrolysis oils) typically contains a mixture of hydrocarbons that could be co-processed with conventional petroleum feedstocks.

[0003] Cracking of hydrocarbons is a process that is widely used to produce olefins and aromatics. Steam cracking is one technique that produces olefins and aromatics by thermal
20 cracking of petroleum feedstocks in the presence of steam at elevated temperatures. Typically, the feedstock for steam cracking may include gaseous or liquid hydrocarbons, such as naphtha, vacuum gas oils, crude oil, and natural gas liquids (e.g., liquefied petroleum gas, condensate, ethane, propane, butane, etc.), among others. Even though recycle pyrolysis oils contain a mixture of hydrocarbons, there may be drawbacks to their use in a cracking process. For
25 example, plastic waste can contain a variety of contaminants (e.g., chlorides, fluorides, bromides, phosphorous-containing compounds, nitrogen, oxygenates, etc.) that can make their use in cracking challenging as the recycle pyrolysis oil can also contain similar contaminants. Conventional cracking processes can be sensitive to many contaminants contained in the recycle pyrolysis oil. For example, these contaminants can cause metallurgical fouling, catalyst
30 poisoning, and/or other problems in the cracking furnace or other downstream units that would result in expensive and time-consuming remedial operations should these recycle pyrolysis oils be used in cracking processes.

SUMMARY

[0004] Disclosed herein is an example method that may include contacting a recycle pyrolysis oil with water to produce a purified pyrolysis oil. The method further may include cracking the purified pyrolysis oil to produce a product.

- 5 [0005] Further disclosed herein is an example method that may include reducing the total acid number of a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a TAN, as determined by ASTM D664, of about 1.5 mg KOH/g or less. The method further may include cracking the purified pyrolysis oil to produce a product.

- 10 [0006] Further disclosed herein is an example that may include removing nitrogen from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total nitrogen content of about 850 wppm or less. The method further may include cracking the purified pyrolysis oil to produce a product.

- [0007] Further disclosed herein is an example that may include removing chlorides from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total chloride content of about 150 wppm or less. The method further may include cracking the purified pyrolysis oil to produce a product.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] These drawings illustrate certain aspects of the present disclosure and should not be used to limit or define the disclosure.

- 20 [0009] FIG. 1 is a block diagram illustrating an example method that includes water washing of a recycle pyrolysis oil for feed to a cracker.

[0010] FIG. 2 is a schematic diagram illustrating an example embodiment for water washing a recycle pyrolysis oil.

- 25 [0011] FIG. 3 is a schematic diagram illustrating an example embodiment for water washing a recycle pyrolysis oil.

[0012] FIG. 4 is a schematic diagram illustrating an example embodiment of a feed arrangement to a steam cracking furnace.

[0013] FIG. 5 is a schematic diagram illustrating another example embodiment of a feed arrangement to a steam cracking furnace.

- 30 [0014] FIG. 6 is a schematic diagram illustrating another example embodiment of a feed arrangement to a steam cracking furnace.

[0015] FIG. 7 is a schematic diagram illustrating an example embodiment of a feed arrangement to multiple steam cracking furnaces.

DETAILED DESCRIPTION

[0016] This application relates to cracking hydrocarbons and, more particularly, in one or more embodiments, relates to methods and systems that include water washing of a recycle pyrolysis oil for feed to a cracker. Advantageously, water washing of the recycle pyrolysis oil should reduce contaminants therein, resulting in a suitable feed for subsequent cracking. Without washing, the recycle pyrolysis oil contains a number of contaminants that make its use in cracking problematic. Contaminants in the recycle pyrolysis oil include, but are not limited to, chloride, nitrogen, and oxygenates. As used herein, the term “oxygenate” refers to any chemical compound that contains oxygen as part of its chemical structure. Some oxygenates may include, but are not limited to, alcohols, aldehydes, ketones, and ethers, for example. Pretreatments such as hydrotreatment and thermal dechlorination can be used for contaminant reduction but may add undesirable complexity and cost to make use of the recycle pyrolysis oil in subsequent cracking operations economical.

[0017] FIG. 1 is a simplified block diagram illustrating a system 10 for recycling waste in accordance with some embodiments. As illustrated, the system 10 may include the following units: (i) a pyrolysis unit 12 in which a pyrolysis feed 14 containing a waste is pyrolyzed to form a recycle pyrolysis oil; (ii) a water wash unit 16 that washes a water wash feed 18 comprising the recycle pyrolysis oil to remove contaminants; and (iii) a cracking unit 20 that cracks at least purified pyrolysis oil in a cracker feed 22 from the water wash unit 16. While the recycle pyrolysis oil from the water wash unit 16 is referred to as purified, it is not intended to imply that the water wash unit 16 removes all the contaminants from the recycle pyrolysis oil, but rather that the water wash unit 16 purifies the recycle pyrolysis oil by reducing the content of one or more contaminants. In addition, FIG. 1 is not intended to imply that a direct fluid connection between the pyrolysis unit 12 and the water wash unit 16 and between the water wash unit 16 and the cracking unit 20 is required. Rather, the plastic-derived pyrolysis can be produced at one site and then transported to another site for water washing. Likewise, the purified pyrolysis oil can be produced at one site and transported to another site for cracking.

[0018] The waste fed to the pyrolysis unit 12 may include plastic waste obtained from any source including, but not limited to, municipal, industrial, commercial or consumer sources. In some embodiments, the plastic waste may include post-consumer use plastics. The plastic waste further may be obtained from a common source or from mixed sources, including mixed plastic waste obtained from municipal or regional sources and/or from waste streams of polyethylene terephthalates (PET), high density polyethylene (HDPE), low density

polyethylene (LDPE), linear low density polyethylene (LLDPE), polypropylene, and/or polystyrene. Furthermore, the waste may include thermoplastic elastomers and thermoset rubbers, such as from tires and other articles made from natural rubber, polybutadiene, styrene-butadiene, butyl rubber and ethylene propylene diene monomer rubber (EPDM). The waste that is processed may also include any of various used polymeric and non-polymeric articles without limitation. Some examples of the many types of polymeric articles may include: films (including cast, blown, and otherwise), sheets, fibers, woven and nonwoven fabrics, furniture (e.g., garden furniture), sporting equipment, bottles, food and/or liquid storage containers, transparent and semi-transparent articles, toys, tubing and pipes, sheets, packaging, bags, sacks, coatings, caps, closures, crates, pallets, cups, non-food containers, pails, insulation, and/or medical devices. Further examples include automotive, aviation, boat and/or watercraft components (e.g., bumpers, grills, trim parts, dashboards, instrument panels and the like), wire and cable jacketing, agricultural films, geomembranes, playground equipment, and other such articles, whether blow molded, roto-molded, injection-molded, or the like. Any of the foregoing may include mixtures of polymeric and non-polymeric items (e.g., packaging or other articles may include inks, paperboards, papers, metal deposition layers, and the like). The ordinarily skilled artisan will appreciate that such polymeric articles may be made from any of various polymer and/or non-polymer materials, and that the polymer materials may vary widely (e.g., ethylene-based, propylene-based, butyl-based polymers, and/or polymers based on any C₂ to C₄₀ or even higher olefins, and further including polymers based on any one or more types of monomers, e.g., C₂ to C₄₀ α -olefin, di-olefin, cyclic olefin, etc. monomers). Common examples include ethylene, propylene, butylene, pentene, hexene, heptene, and octene; as well as multi-olefinic (including cyclic olefin) monomers such as ethylidene norbornene (ENB) and vinylidene norbornene (VNB) (including, e.g., when such cyclic olefins are used as comonomers, e.g., with ethylene monomers).

[0019] In some embodiments, the waste may include one or more plastics classified as plastic identification code (PIC) 1 to 7 by the Society of the Plastics Industry. For example, the waste may include one or more of the following plastics: polyethylene terephthalate classified as PIC 1; high-density polyethylene classified as PIC 2; polyvinyl chloride classified as PIC 3; low-density polyethylene classified as PIC 4; polypropylene classified as PIC 5; polystyrene classified as PIC 6; and polycarbonate and other plastics classified as PIC 7. Combinations of the various plastics classified as PIC 1 to 7 may also be used in some embodiments.

[0020] In the pyrolysis unit 12, the pyrolysis feed 14 containing the waste may be pyrolyzed to form a recycle pyrolysis oil. Pyrolysis is a technique of chemical recycling that includes thermal degradation of the waste to produce gas and liquid products, referred to as recycle pyrolysis oil and a recycle pyrolysis gas. As used herein “recycle pyrolysis oil” refers to compositions of matter that are liquid when measured at 25°C and 1 atm, and at least a portion of which are obtained from the pyrolysis of recycled waste (e.g., recycled plastic waste). As used herein “recycle pyrolysis gas” refers to compositions of matter that are a gas at 25°C and 1 atm, and at least a portion of which are obtained from the pyrolysis of recycled waste. In some embodiments, the waste may be heated in an environment free (or substantially free) of oxygen. For example, the pyrolysis may occur in an environment that includes 5 weight percent oxygen or less, 3 weight percent oxygen or less, 1 weight percent oxygen or less, or 0.5 weight percent oxygen or less. The pyrolysis products may depend on a number of factors, including, but not limited to, pyrolysis reactor temperature, pyrolysis reactor pressure, reactor residence time, and process configuration. An example pyrolysis technique for producing a recycle pyrolysis oil is described in U.S. Patent No. 10,131,847, the entire disclosure of which is incorporated herein by reference. The pyrolysis unit 12 can include a variety of different equipment suitable for pyrolysis of waste, including but not limited to, reactors, extruders, tanks, vessels, valves, sensors, hoppers, conveyance systems, and piping, among others.

[0021] A specific pyrolysis technique will now be described in more detail. In an example embodiment, a waste (e.g., a plastic waste) may be provided, for example, in a granular, flake, or pellet form, and fed to the pyrolysis unit 12. In the pyrolysis unit 12, the waste may be melted to produce a molten liquid (e.g., molten plastic). For example, the waste may be melted in an extruder to a temperature of 300°C to 320°C. The molten liquid may then be pyrolyzed in an environment free (or substantially free) of oxygen to produce pyrolysis gases. For example, the molten liquid may be heated in pyrolysis chamber to a higher temperature, such as 390°C to about 410°C, while agitating. Long chain hydrocarbons (e.g., approximately 30 carbon atoms or longer) in the produced pyrolysis gases may then be condensed and further pyrolyzed for further thermal degradation while shorter chain hydrocarbons may exit in gaseous form. For example, the produced pyrolysis gases may be directed to a contactor for contact with a bank of condenser elements (e.g., plates) upon which the long chain hydrocarbons may condense. The long chain hydrocarbons may flow from the condenser back to the pyrolysis chamber. The pyrolysis gases including the shorter chain hydrocarbons may be distilled in a distillation column to provide recycle pyrolysis gas and recycle pyrolysis oil.

- [0022] As previously described, the pyrolysis unit 12 produces a recycle pyrolysis oil. The particular composition and properties of the recycle pyrolysis oil will vary based on a number of factors, including the pyrolysis conditions, the pyrolysis technique, and the initial waste. The recycle pyrolysis oil may include hydrocarbons, such as paraffins, aromatics, naphthalenes, and olefins. In some embodiments, the recycle pyrolysis oil may include 90% or greater of hydrocarbons having at least 5 carbon atoms. For example, the recycle pyrolysis oil may include hydrocarbons having at least 5 carbon atoms in an amount of 90% by weight, 95% by weight, 98% by weight, 99% by weight, or greater. In some embodiments, the recycle pyrolysis oil may comprises olefins in an amount of 50% by weight or less. For example, the recycle pyrolysis oil may comprises olefins in an amount of 0.1% by weight to 50% by weight, 0.1% by weight to 40% by weight, 0.1% by weight to 25% by weight, 0.1 % by weight to 10% by weight, or 10% by weight to 20% by weight, 20% by weight to 30% by weight, 30% by weight to 40% by weight, or 30% by weight to 50% by weight. In some embodiments, the recycle pyrolysis oil may comprises aromatic in an amount of 25% by weight or less. For example, the recycle pyrolysis oil may comprises aromatics in an amount of 0.1% by weight to 25% by weight, 0.1% by weight to 15% by weight, 0.1 % by weight to 10% by weight, or 10% by weight to 20% by weight, 20% by weight to 25% by weight. However, it should be understood that a particular recycle pyrolysis oil may have concentrations of components outside these disclosed ranges.
- [0023] The recycle pyrolysis oil may have any suitable API gravity as desired for a particular application. As used herein, the term “API gravity” is a measure of how heavy or light an oil is as compared to water as measured in accordance with ASTM D4052. In some embodiments, the recycle pyrolysis oil may have an API gravity of 25 to 75, 25 to 65, 25 to 50, 30 to 70, 50 to 75, or 30 to 65.
- [0024] In some embodiments, the recycle pyrolysis oil may have a final boiling point of 600°C or less. As used herein, the final boiling point is the temperature at which the highest boiling point compounds evaporate as determined in accordance with ASTM 2887. In some embodiments, the recycle pyrolysis oil may have a final boiling point of 400°C to 600°C, 450°C to 600°C, 500°C to 600°C, 550°C to 600°C, 400°C to 550°C, 450°C to 550°C, 450°C to 500°C, or 500°C to 550°C.
- [0025] In some embodiments, the recycle pyrolysis oil may have a kinematic viscosity at 40°C (“KV40”) of 2 centistokes (cSt) or less. As used herein, the terms “kinematic viscosity at 40°C” or “KV40” of an oil refers to the kinematic viscosity at 40°C as measured in accordance with ASTM D445.

[0026] The recycle pyrolysis oil can contain a number of contaminants at elevated levels making it unsuitable for further processing, such as cracking, to produce more valuable products. For example, the recycle pyrolysis oil can contain nitrogen, chlorides, fluorine and fluorine containing compounds, bromine and bromine containing compounds, phosphorous and phosphorous containing compounds, and oxygenates including, but not limited to, 5 alcohols, aldehydes, ketones, and ethers, for example, in levels that makes further processing challenging. In some embodiments, the recycle pyrolysis oil may have a total nitrogen content of 860 weight parts per million (wppm) or greater. For example, the recycle pyrolysis oil (wppm) may have a total nitrogen content of 860 wppm to 3000 wppm, 900 wppm to 2000 10 wppm, 900 wppm to 1500 wppm, or 900 wppm to 1400 wppm. As used herein, the total nitrogen content is the sum of measure of the total nitrogen species in the recycle pyrolysis oil, as determined in accordance with ASTM D5762. The recycle pyrolysis oil may have a total chlorides content of 160 wppm or greater. For example, the recycle pyrolysis oil may have a total chlorides content of 170 wppm to 300 wppm, 170 wppm to 275 wppm, 170 wppm to 250 15 wppm, 200 wppm to 300 wppm, or 200 wppm to 250 wppm. As used herein, the total chlorides content is the sum of measure of the total chlorides (organic and inorganic) in the recycle pyrolysis oil, as determined in accordance with ASTM D7359. The recycle pyrolysis oil may have contain fluorine and/or fluorine containing compounds in an amount of 1 wppm to 1000 wppm or greater. Alternatively, the recycle pyrolysis oil may have contain fluorine and/or 20 fluorine containing compounds in an amount of 1 wppm to 10 wppm, in an amount of 10 wppm to 100 wppm, in an amount of 100 wppm to 500 wppm, in an amount of 500 wppm to 1000 wppm, or any ranges therebetween. The recycle pyrolysis oil may have contain bromine and/or bromine containing compounds in an amount of 1 wppm to 1000 wppm or greater. Alternatively, the recycle pyrolysis oil may have contain bromine and/or bromine containing 25 compounds containing compounds in an amount of 1 wppm to 10 wppm, in an amount of 10 wppm to 100 wppm, in an amount of 100 wppm to 500 wppm, in an amount of 500 wppm to 1000 wppm, or any ranges therebetween. The recycle pyrolysis oil may have contain phosphorous and/or phosphorous containing compounds in an amount of 1 wppm to 1000 wppm or greater. Alternatively, the recycle pyrolysis oil may have contain phosphorous and/or 30 phosphorous containing compounds containing compounds in an amount of 1 wppm to 10 wppm, in an amount of 10 wppm to 100 wppm, in an amount of 100 wppm to 500 wppm, in an amount of 500 wppm to 1000 wppm, or any ranges therebetween. While oxygenates (e.g., alcohols, ethers, and other species containing oxygen) in the recycle pyrolysis oil may be challenging to accurately quantify, there presence may be problematic in subsequent

processing, for example, with increased carbon monoxide and carbon dioxide product in subsequent cracking operations. In some embodiments, the recycle pyrolysis oil may have contain oxygenates in an amount of 1 wppm to 10 wppm, in an amount of 10 wppm to 100 wppm, in an amount of 100 wppm to 500 wppm, in an amount of 500 wppm to 1000 wppm, or any ranges therebetween.

[0027] In addition to specific concentrations of contaminants, certain contaminants can cause the recycle pyrolysis oil to have a high acidity that can be problematic for further processing. The total acid number, as determined in accordance with ASTM D664, is a measurement that can be used to quantify the acidity of the recycle pyrolysis oil. The recycle pyrolysis oil may have a total acid number of 1.7 mg KOH/g or greater. In some embodiments, the recycle pyrolysis oil may have a total acid number of 1.7 mg KOH/g to 4 mg KOH/g, 1.7 mg KOH/g to 3 mg KOH/g, 1.7 mg KOH/g to 2.5 mg KOH/g, 2 mg KOH/g to 4 mg KOH/g, 2 mg KOH/g to 3 mg KOH/g, or 2 mg KOH/g to 2.5 mg KOH/g.

[0028] With continued reference to FIG. 1, the system 10 further includes the water wash unit 16 to reduce contaminants in the recycle pyrolysis oil. The water wash unit 16 receives a water wash feed 18 from the pyrolysis unit 12, wherein the water wash feed 18 includes the recycle pyrolysis oil. In the water wash unit 16, the recycle pyrolysis oil is contacted with water to produce a purified pyrolysis oil. For example, the water wash unit 18 may include mixing of the recycle pyrolysis oil with water for selective transfer of certain solutes from the recycle pyrolysis oil to the water, thus extracting contaminants from the recycle pyrolysis oil to produce. The recycle pyrolysis oil and the water may then be allowed to separate producing a water phase and a phase of a purified pyrolysis oil.

[0029] The contact of the recycle pyrolysis oil and water in the water wash unit 16 can occur at any of a variety of suitable conditions to achieve a desirable level of contaminant reduction. For example, the contact may occur at a weight ratio of recycle pyrolysis oil to water of 0.1:1 to 3:1. By way of further example, the contact may occur at temperature of 10°C to 100°C. By way of further example, the contact may occur at a pressure of ambient to 2100 kPA.

[0030] The water used in the water wash unit 16 may be any suitable water for removing contaminants from the recycle pyrolysis oil, including but not limited to, fresh water, deionized water, and demineralized water, among others. In some embodiments, the water may have a neutral or basic pH. For example, the water may have a pH of 7 to 13, 7 to 12, 7 to 10, 7 to 9, or any ranges therebetween. In particular embodiments, the water may be neutral with pH of 7. In embodiments, the water may be acidic. For example, the water may have a pH of 4

to 7, a pH of 4 to 6, a pH of 4 to 5, or any ranges therebetween. In embodiments where the recycle pyrolysis oils contains acidic contaminants, the water used may be neutral to basic. In embodiments where the recycle pyrolysis oil contains basic contaminants, the water used may be neutral to acidic.

5 **[0031]** The water wash unit 16 may have any of a variety of configurations suitable for liquid-liquid extraction. For example, the water wash unit 16 may utilize a mixer-settler, a column, or a centrifugal contactor. The water wash unit 16 may include any of a variety of different equipment to facilitate contact between the water and recycle pyrolysis oil, including, but not limited to, mixers, tanks, centrifugal contactors, vessels, columns, valves,
10 sensors, and piping, among others.

[0032] FIG. 2 illustrates an example embodiment of the water wash unit 16 for washing the recycle pyrolysis oil in accordance with example embodiments. As illustrated, the water wash unit 16 may receive a water wash feed 18. Water from water feed 22 at a rate regulated by valve 24 may combine with the recycle pyrolysis oil in the water wash feed 18 which then
15 enters a wash drum 26 after passing through a mixing device 28. While the water and recycle pyrolysis oil are shown as combining prior to feed to the mixing device 28, the water and the recycle pyrolysis oil may be otherwise fed to the mixing device 28, for example, they may be separately fed to the mixing device 28. In addition, the mixing device 28, while shown as a separate component may be otherwise configured, for example, the mixing device 28 may
20 be integrated into the wash drum 26 with the wash drum 26 having a mixing section (not shown) and settling section (not shown). Any suitable mixing device 28 may be used for facilitating contact between the water and the recycle pyrolysis oil, including, but not limited to, paddle mixers and inline mixers, among others. In the wash drum 26, a two-phase separation occurs between the water and the recycle pyrolysis oil to produce a purified
25 pyrolysis oil and water containing extracted contaminants from the recycle pyrolysis oil. The purified pyrolysis oil may be removed from the wash drum 26 via line 30 at a rate controlled by valve 32. The water containing extracted contaminants may be removed from the wash drum 26 via line 34 at a rate controlled by valve 36. While FIG. 2, illustrates single stage separation, it should be understood that example embodiments may use multiple extraction
30 stages, for example, by arrangement of multiple of the mixing device 28 and the wash drum 26 in series.

[0033] FIG. 3 illustrates another example embodiment of the water wash unit 16 for washing the recycle pyrolysis oil in accordance with example embodiments. As illustrated, the water wash unit 16 may receive a water wash feed 18. The water wash feed 18 containing

the recycle pyrolysis oil may be fed to a wash tower 38 at a rate controlled by valve 40. Water from the water feed 22 may be introduced to the wash tower 38 at a rate controlled by valve 42 to contact the recycle pyrolysis oil. By contact with the recycle pyrolysis oil in the wash tower 38, the water should remove contaminants therefrom. The wash tower 38 may include
5 a working section 44 that can contain packing or trays, for example, to facilitate the water and recycle pyrolysis oil contact. The water and the recycle pyrolysis oil may flow counter-currently through the wash tower to produce a purified pyrolysis oil, which may be removed from the wash tower 38 via line 46 at a rate controlled by valve 48. The water containing extracted contaminants may be removed from the wash tower 38 via line 50 at a rate
10 controlled by valve 52.

[0034] As previously described, the water wash unit 16 should remove contaminants from the recycle pyrolysis oil to produce a purified pyrolysis oil suitable for further processing. For example, the purified pyrolysis oil may have a total nitrogen content of 850 wppm or less. In some embodiments, the purified pyrolysis oil may have a total nitrogen content of 200
15 wppm to 850 wppm, 400 wppm to 850 wppm, 500 wppm to 850 wppm, 600 wppm to 850 wppm, 200 wppm to 800 wppm, 200 wppm to 600 wppm, 400 wppm to 850 wppm, 400 wppm to 800 wppm, or 400 wppm to 600 wppm. In some embodiments, the total nitrogen content in the recycle pyrolysis oil may be reduced by the water wash in an amount of at least 15%, at least 30%, at least 40%, at least 50%, or at least 60%. By way of further example, the purified
20 pyrolysis oil may have a total chlorides content of 150 wppm or less. In some embodiments the purified pyrolysis oil may have a total chlorides content of 50 wppm to 150 wppm, 75 wppm to 150 wppm, 100 wppm to 150 wppm, 50 wppm to 140 wppm, 75 wppm to 140 wppm, or 100 wppm to 140 wppm.

[0035] In some embodiments, the purified pyrolysis oil may have a total fluorine and/or
25 fluorine containing compound content of 850 wppm or less. In some embodiments, the purified pyrolysis oil may have a total fluorine and/or fluorine containing compound of 200 wppm to 850 wppm, 400 wppm to 850 wppm, 500 wppm to 850 wppm, 600 wppm to 850 wppm, 200 wppm to 800 wppm, 200 wppm to 600 wppm, 400 wppm to 850 wppm, 400 wppm to 800 wppm, or 400 wppm to 600 wppm. In some embodiments, the total fluorine and/or fluorine
30 containing compound in the recycle pyrolysis oil may be reduced by the water wash in an amount of at least 15%, at least 30%, at least 40%, at least 50%, or at least 60%.

[0036] In some embodiments, the purified pyrolysis oil may have a total bromine and/or bromine containing compound content of 850 wppm or less. In some embodiments, the purified pyrolysis oil may have a total bromine and/or bromine containing compound of 200 wppm to

850 wppm, 400 wppm to 850 wppm, 500 wppm to 850 wppm, 600 wppm to 850 wppm, 200 wppm to 800 wppm, 200 wppm to 600 wppm, 400 wppm to 850 wppm, 400 wppm to 800 wppm, or 400 wppm to 600 wppm. In some embodiments, the total bromine and/or bromine containing compound in the recycle pyrolysis oil may be reduced by the water wash in an amount of at least 15%, at least 30%, at least 40%, at least 50%, or at least 60%.

[0037] In some embodiments, the purified pyrolysis oil may have a total phosphorous and/or phosphorous containing compound content of 850 wppm or less. In some embodiments, the purified pyrolysis oil may have a total phosphorous and/or phosphorous containing compound of 200 wppm to 850 wppm, 400 wppm to 850 wppm, 500 wppm to 850 wppm, 600 wppm to 850 wppm, 200 wppm to 800 wppm, 200 wppm to 600 wppm, 400 wppm to 850 wppm, 400 wppm to 800 wppm, or 400 wppm to 600 wppm. In some embodiments, the total phosphorous and/or phosphorous containing compounds in the recycle pyrolysis oil may be reduced by the water wash in an amount of at least 15%, at least 30%, at least 40%, at least 50%, or at least 60%.

[0038] In some embodiments, the total chloride content in the recycle pyrolysis oil may be reduced by the water wash in an amount of at least 20%, at least 30%, at least 40%, at least 50%, or at least 60%. By way of further example, the purified pyrolysis oil may have a total acid number of 1.5 mg KOH/g or less. In some embodiments, the purified pyrolysis oil may have a total acid number of 0.5 mg KOH/g to 1.5 mg KOH/g, 0.75 mg KOH/g to 1.5 mg KOH/g, 1 mg KOH/g to 1.5 mg KOH/g, 0.5 mg KOH/g to 1.4 mg KOH/g, 0.75 mg KOH/g to 1.4 mg KOH/g, or 1 mg KOH/g to 1.4 mg KOH/g. In some embodiments, the total acid number of the recycle pyrolysis oil may be reduced by the water wash in an amount of 20% or greater, 30% or greater, 40% or greater, 50% or greater, or 50% or greater. In addition, while removal of oxygenates can be challenging to directly quantify, their removal can be indicated by a reduction in carbon monoxide and carbon dioxide generation in subsequent cracking when the recycle pyrolysis has been water washed.

[0039] Referring to FIG. 1, the system 10 further includes the cracking unit 20 that receives a cracker feed 22 containing the purified pyrolysis oil from the waste wash unit 16. In the cracking unit 20, longer chain hydrocarbons in the purified pyrolysis oil are broken down into smaller hydrocarbons, including, but not limited to, olefins (e.g., ethylene, propylene, butylenes), aromatics (e.g., benzene, toluene, xylene), and molecular hydrogen (H₂), or any combination thereof. Any suitable technique for cracking of the purified pyrolysis oil can be used. Examples of suitable techniques may include, but are not limited to, thermal cracking, steam cracking, flexicoking, delayed coking, and fluid catalytic cracking. The cracking unit 20 may

include any of a variety of different equipment to facilitate cracking as well as subsequent separation and clean up, including, but not limited to, furnaces, columns, vessels, sensors, and piping, among others.

[0040] In some embodiments, steam cracking may be used in the cracking unit 20 for converting the purified pyrolysis oil to olefins. Steam cracking is a technique that can be used to thermally crack various hydrocarbons into lighter hydrocarbons, such as olefins and aromatics. Conventional steam cracking techniques utilize a steam cracking furnace that includes two sections: a convection section and a radiant (or pyrolysis) section. In accordance with example embodiments, the purified pyrolysis oil enters the convection section of the steam cracking furnace where it is heated by indirect contact with hot flue gas from the radiant section and by direct contact with steam. In the convection section, the purified pyrolysis oil may be heated to a temperature of 100°C or greater. For example, the purified pyrolysis oil may be heated to a temperature of 100° to 650°C, 100° to 500°C, 100° to 450°C, 100° to 400°C, 200° to 650°C, 300° to 650°C, 400° to 650°C, 500° to 650°C, 400° to 600°C, 400° to 500°C, or 300° to 500°C. The purified pyrolysis oil and steam may be fed into the steam cracking furnace at any suitable purified pyrolysis oil to steam weight ratio, including a weight ratio of purified pyrolysis oil to steam of 1:0.1 to 1:2 (e.g., 1:0.1 to 1:0.5, 1:0.75 to 1:0.5, or 1:1 to 1:0.5).

[0041] The mixture of hydrocarbons and steam is then introduced into the radiant section of the steam cracking furnace where thermal cracking occurs. In the radiant section, the mixture can be heated to a temperature of 950°C, for example, including temperatures of 400° to 950°C, 400° to 900°C, 400° to 750°C, 700° to 900°C, or 750° to 900°C. The radiant section may have any suitable pressure for cracking, including, but not limited to, a pressure of 0.1 bar absolute to 5 bar absolute, 1 bar absolute to 5 bar absolute, or 2 bar absolute to 5 bar absolute. The radiant section may have any suitable residence time for cracking, including, but not limited to, a residence time of 0.1 seconds to 2 seconds, 0.5 to 1 second, or 1 second to 2 seconds. The cracker effluent leaves the steam cracking furnace for further downstream processing, including quenching. Quenching can be desirable to cool the cracking effluent and prevent further reactions. Cooling can be carried out, for example, transfer line exchanger for steam generation or in a quench point or quench pipe for receiving the cracker effluent.

[0042] In some embodiments, the purified pyrolysis oil can be cracked in the presence of a hydrocarbon co-feed in the cracking unit 20. By blending with the hydrocarbon co-feed, any remaining contaminants in the purified pyrolysis oil may be further diluted. For example, the purified pyrolysis oil can be steam cracked in a steam cracking furnace in the presence of a hydrocarbon co-feed. The purified pyrolysis oil can be admixed before or after introduction

into the steam cracking furnace to yield a mixed feed that is then cracked. Suitable hydrocarbon co-feeds may include any of a variety of hydrocarbon steam cracker feeds that can be cracked in a steam cracker. Examples of suitable hydrocarbon co-feeds may include, but are not limited to, ethane, propane, butane, asphaltenes, resid (e.g., atmospheric resid, vacuum resid), pitch, crude oil, naphtha, gas oil (e.g., vacuum gas oil, heavy gas oil), liquefied petroleum gas, condensate, one or more other hydrocarbons, or combinations thereof. In some embodiments, there may be more than one hydrocarbon co-feed, for example, a first hydrocarbon co-feed may be combined with the purified pyrolysis oil for cracking while a second hydrocarbon co-feed may be simultaneously cracked in the same (or a different steam cracking furnace) while segregated from the purified pyrolysis oil. The second hydrocarbon co-feed that is segregated may be the same or different than the first hydrocarbon co-feed that is combined with the purified pyrolysis oil. For example, the first hydrocarbon co-feed combined with the purified pyrolysis oil may be a heavier hydrocarbon liquid (e.g., gasoil) than the second hydrocarbon co-feed (e.g., butane, naphtha) that is segregated.

[0043] The purified pyrolysis oil and the hydrocarbon co-feed can be combined at any suitable ratio. For example, the purified pyrolysis oil and the hydrocarbon co-feed may be combined at a purified pyrolysis oil and hydrocarbon co-feed weight ratio of 1:100 to 1:1.5, including, but not limited to weight ratios of, 1:50 to 1:1.5, 1:25 to 1:1.5, 1:20 to 1:1.5, 1:100 to 1:5, 1:100 to 1:4, 1:100 to 1:10, 1:50 to 1:5, or 1:20 to 1:5. In addition, where combined with a co-feed, the mixture of the purified pyrolysis oil and the hydrocarbon co-feed may be fed with steam to the steam cracker furnace at any suitable ratio, including a weight ratio of the mixture to steam of 1:0.1 to 1:2 (e.g., 1:0.1 to 1:0.5, 1:0.75 to 1:0.5, or 1:1 to 1:0.5). The co-feed may include the purified pyrolysis oil in an amount of 0.1 wt.% to 50 wt.%. Alternatively, the co-feed may include the purified pyrolysis oil in an amount of 0.1 wt.% to 1 wt.%, in an amount of 1 wt.% to 5 wt.%, in an amount of 5 wt.% to 10 wt.%, in an amount of 10 wt.% to 15 wt.%, in an amount of 15 wt.% to 20 wt.%, in an amount of 20 wt.% to 25 wt.%, in an amount of 25 wt.% to 30 wt.%, in an amount of 30 wt.% to 35 wt.%, in an amount of 35 wt.% to 40 wt.%, in an amount of 40 wt.% to 45 wt.%, in an amount of 45 wt.% to 50 wt.%, or any ranges therebetween. The co-feed may include the hydrocarbon co-feed in an amount of 0.1 wt.% to 50 wt.%. Alternatively, the co-feed may include the hydrocarbon co-feed in an amount of 0.1 wt.% to 1 wt.%, in an amount of 1 wt.% to 5 wt.%, in an amount of 5 wt.% to 10 wt.%, in an amount of 10 wt.% to 15 wt.%, in an amount of 15 wt.% to 20 wt.%, in an amount of 20 wt.% to 25 wt.%, in an amount of 25 wt.% to 30 wt.%, in an amount

of 30 wt.% to 35 wt.%, in an amount of 35 wt.% to 40 wt.%, in an amount of 40 wt.% to 45 wt.%, in an amount of 45 wt.% to 50 wt.%, or any ranges therebetween.

[0044] FIG. 4 is a schematic diagram illustrating an example embodiment of a feed arrangement to a steam cracking furnace 54. The steam cracking furnace 54 may include a convection section 56 and a radiant section 58. As illustrated, the cracker feed 22 containing the purified pyrolysis oil may be feed into the convection section 56. In the illustrated embodiment, the purified pyrolysis oil in cracker feed 22 may admixed with a hydrocarbon co-feed from line 60 to form a mixed feed. In some embodiments, the purified pyrolysis oil and hydrocarbon co-feed can be admixed before entering the convection section 56 with the mixed feed then entering the convection section 56 of the steam cracking furnace 54. This mixed feed of the purified pyrolysis oil and hydrocarbon co-feed may traverse through the convection section 56 through a series of tubes 62. Flue gas from the radiant section 58 travels upward through the convection section 56 to heat the tubes 62 and contents thereof, thus preheating the mixed feed. The mixed feed of the purified pyrolysis oil and hydrocarbon co-fed in the convection section 56 may be diluted with steam fed into the tubes 62 in the convection section by line 64. This diluted mixture may then be fed to the radiant section 58 in the tubes 62 where it is cracked with the cracker effluent being removed from the radiant section 58 by way of an effluent line 66. As previously mentioned, the cracker effluent may include cracker products, including, not limited to, olefins and/or aromatics.

[0045] FIG. 5 is a schematic diagram illustrating another example embodiment of a feed arrangement to the steam cracking furnace 54. In a similar manner to the embodiment of FIG. 4, the illustrated embodiment of FIG. 5 includes a steam cracking furnace 54 that receives into the convection section 56 a cracker feed 22 that includes the purified pyrolysis oil. As illustrated, the purified pyrolysis oil may be admixed with a hydrocarbon co-feed from line 60 such that a mixed feed traverses through the convection section 56 to the radiant section 58 by way of tubes 62. Prior to the radiant section 58, the mixed feed of the purified pyrolysis oil and hydrocarbon co-feed is diluted by steam from line 64 and then the diluted mixture is cracked in the radiant section 58 with a cracker effluent being removed from the radiant section 58 by way of the effluent line 66. However, in addition to the purified pyrolysis oil and the hydrocarbon co-feed, a second hydrocarbon co-feed may also be fed into the convection section 56. As illustrated, a second cracker feed 67 that includes a second hydrocarbon co-feed may be introduced to the convection section 56 where it traverses through the convection section 56 to the radiant section 58 through a series of second tubes 68. In the illustrated embodiment, the second hydrocarbon co-feed in the second tubes 68 may be segregated from the purified

pyrolysis oil as it traverses through the steam cracking furnace 54. Flue gas from the radiant section 58 travels upward through the convection section 56 to heat the tubes 68 and contents thereof, thus preheating the second hydrocarbon co-feed. The second hydrocarbon co-feed in the convection section 56 may be diluted with additional steam fed into the tubes 68 in the convection section by line 70. This diluted second co-feed may then be fed to the radiant section 58 in the tubes 68 where it is cracked with the additional cracker effluent being removed from the radiant section 58 by way of a second effluent line 72. This additional cracker effluent may include cracker products, including, not limited to, olefins and/or aromatics.

[0046] FIG. 6 is a schematic diagram illustrating another example embodiment of a feed arrangement to the steam cracking furnace 54. In a similar manner to the embodiment of FIG. 4, the illustrated embodiment of FIG. 5 includes a steam cracking furnace 54 with a cracker feed 22 that includes the purified pyrolysis oil. As illustrated, the cracker feed 22 with the purified pyrolysis oil traverse through tubes 62 to the radiant section 58 of the steam cracking furnace 54. In addition, a hydrocarbon co-feed is also introduced to the steam cracking furnace 54. However, instead of being admixed before feed into the steam cracking furnace 54, the hydrocarbon co-feed and the purified pyrolysis oil are admixed in tubes 62 of the steam cracking furnace 54. As illustrated, the hydrocarbon co-feed may be fed to the convection section 56 of the steam cracking furnace 54 by way of line 60. The purified pyrolysis oil may be fed to the steam cracking furnace 54 by way of cracker feed 22. In the illustrated embodiment, there are multiple potential feed locations of the cracker feed 22 to the steam cracking furnace 54, illustrated on FIG. 5, as cracker feed 22a, cracker feed 22b, cracker feed 22c, and cracker feed 22d. Each of the different potential feed locations is downstream of the feed location of line 60 with the hydrocarbon co-feed with cracker feed 22a and cracker feed 22b being upstream of the feed location of the steam and cracker feed 22c and cracker feed 22d being downstream of the feed location of the steam. Flue gas from the radiant section 58 travels upward through the convection section 56 to heat the tubes 62 and contents thereof, thus preheating the purified pyrolysis oil and hydrocarbon co-feed. The purified pyrolysis oil and hydrocarbon co-feed in the convection section 56 may be diluted with steam fed into the tubes 62 in the convection section by line 64. A diluted mixture of the steam, purified pyrolysis oil, and hydrocarbon co-feed may be fed to the radiant section 58 in the tubes 62 where it is cracked with the cracker effluent being removed from the radiant section 58 by way of an effluent line 66. As previously mentioned, the cracker effluent may include cracker products, including, not limited to, olefins and/or aromatics.

[0047] FIG. 7 is a schematic diagram illustrating an example embodiment of a feed arrangement to multiple steam cracking furnaces. In the illustrated embodiments, three steam cracking furnaces are shown, identified as first steam cracking furnace 74, second steam cracking furnace 76, and third steam cracking furnace 78. As illustrated, a cracker feed 22 that includes a purified pyrolysis oil may be provided and combined with a hydrocarbon co-feed from line 60 to yield a mixed co-feed. The cracker feed 22 may then be split into a first cracker feed 80 and a second cracker feed 82. The first cracker feed 80 containing the mixed co-feed may be fed into the first steam cracking furnace 74 where it is diluted with steam from first cracker steam line 84 and then cracked with a first cracker effluent being removed from the first steam cracking furnace 74 by way of first cracker effluent line 86. The second cracker feed 82 containing the mixed co-feed may be fed into the second steam cracking furnace 76 where it is diluted with steam from second cracker steam line 88 and then cracked with a second cracker effluent being removed from the second steam cracking furnace 76 by way of second cracker effluent line 90. A separate hydrocarbon feed stream may also be provided and fed to the third steam cracking furnace 78 by way of line 92. The separate hydrocarbon feed stream may include any of the previously described co-feeds and may be the same or different than the hydrocarbon co-feed admixed with the purified pyrolysis oil. In the third steam cracking furnace 78, the second hydrocarbon feed stream from line 92 may be diluted with steam from third cracker steam line 94 and then cracked with a third cracker effluent being removed from the third steam cracking furnace 78 by way of the third cracker effluent line 96. In each of the steam cracking furnaces, products in the effluents may include, but are not limited to, olefins and aromatics.

[0048] Accordingly, the present disclosure may provide methods and systems that include water washing of a recycle pyrolysis oil for feed to a cracker. The following are non-limiting example embodiments according to the present disclosure.

[0049] An example embodiment of the present method is a method including: contacting a recycle pyrolysis oil with water to produce a purified pyrolysis oil; and cracking the purified pyrolysis oil to produce a product. This example embodiment may include one or more of the following: Element 1: contacting the recycle pyrolysis oil with water to yield the purified pyrolysis oil; Element 2: cracking the purified pyrolysis oil to produce a product comprises steam cracking the purified pyrolysis oil in the presence of steam; Element 3: wherein cracking the purified pyrolysis oil is performed in the presence of a hydrocarbon co-feed; Element 4: admixing the purified pyrolysis oil with the co-feed to yield a mixed feed; and cracking the mixed feed; Element 5: wherein the cracking the mixed feed is performed in a steam cracking

furnace, and wherein the method comprises cracking a second hydrocarbon feed in the steam cracking furnace, wherein the second hydrocarbon feed is segregated from the purified pyrolysis oil in the steam cracking furnace; Element 6: wherein the hydrocarbon co-feed is heavier than the second hydrocarbon feed that is segregated; Element 7: wherein the cracking the purified pyrolysis oil is performed in a steam cracking furnace, wherein the purified pyrolysis oil and the hydrocarbon co-feed are separately fed to the steam cracking furnace; Element 8: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the hydrocarbon co-feed; Element 9: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the steam; Element 10: wherein the hydrocarbon co-feed and the purified pyrolysis oil are present in a purified pyrolysis oil to hydrocarbon co-feed weight ratio of about 1:100 to about 1:2; Element 11: admixing the purified pyrolysis oil with the hydrocarbon co-feed to yield a mixed feed; cracking the mixed feed in at least first and second steam cracker furnaces to yield a first product; and cracking a separate hydrocarbon feed stream to yield a second product. Element 12: wherein the hydrocarbon co-feed comprises at least one hydrocarbon selected from the group consisting of ethane, propane, butane, asphaltenes, resid, pitch, crude oil, naphtha, gas oil, liquefied petroleum gas, condensate, and combinations thereof; Element 13: removing oxygen-containing compounds from the recycle pyrolysis oil; Element 14: removing methanol from the recycle pyrolysis oil; Element 15: wherein the product comprises at least one hydrocarbon selected from the group consisting of an olefin, an aromatic, and combinations thereof; Element 16: wherein the recycle pyrolysis oil comprises about 95% by weight or greater of hydrocarbons having at least 5 carbon atoms, wherein the recycle pyrolysis oil comprises olefins in an amount of about 50% by weight or less, wherein the recycle pyrolysis oil comprises aromatic in an amount of about 20% by weight or less, and wherein the recycle pyrolysis oil has a final boiling point of about 400°C to about 600°C; Element 17: wherein the water has a pH of about 7 to about 10; Element 18: wherein the TAN of the purified pyrolysis oil is about 0.5 to about 1.5 mg KOG/g, as determined by ASTM D664, wherein the total nitrogen content of the purified pyrolysis oil is about 400 wppm to about 850 wppm, and wherein the total chloride content of the purified pyrolysis oil is about 75 wppm to about 150 wppm; Element 19: wherein the recycle pyrolysis oil is at least partially derived from plastic waste; Element 20: wherein the recycle pyrolysis oil is at least partially derived from post-consumer use plastics. Element 21: wherein the recycle pyrolysis oil further comprises at least one additional contaminant selected from the group consisting of fluorine, a fluorine containing compound, bromine, a bromine containing compound, phosphorous, a phosphorous containing compound, and combinations thereof, and wherein the method further

comprises removing at least a portion of the at least one additional contaminant from the pyrolysis oil.

[0050] Another example embodiment of the present disclosure is a method including: reducing the total acid number of a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a TAN, as determined by ASTM D664, of about 1.5 mg KOH/g or less; and cracking the purified pyrolysis oil to produce a product. This example embodiment may include one or more of the of the following: Element 1: contacting the recycle pyrolysis oil with water to yield the purified pyrolysis oil; Element 2: cracking the purified pyrolysis oil to produce a product comprises steam cracking the purified pyrolysis oil in the presence of steam; Element 3: wherein cracking the purified pyrolysis oil is performed in the presence of a hydrocarbon co-feed; Element 4: admixing the purified pyrolysis oil with the co-feed to yield a mixed feed; and cracking the mixed feed; Element 5: wherein the cracking the mixed feed is performed in a steam cracking furnace, and wherein the method comprises cracking a second hydrocarbon feed in the steam cracking furnace, wherein the second hydrocarbon feed is segregated from the purified pyrolysis oil in the steam cracking furnace; Element 6: wherein the hydrocarbon co-feed is heavier than the second hydrocarbon feed that is segregated; Element 7: wherein the cracking the purified pyrolysis oil is performed in a steam cracking furnace, wherein the purified pyrolysis oil and the hydrocarbon co-feed are separately fed to the steam cracking furnace; Element 8: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the hydrocarbon co-feed; Element 9: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the steam; Element 10: wherein the hydrocarbon co-feed and the purified pyrolysis oil are present in a purified pyrolysis oil to hydrocarbon co-feed weight ratio of about 1:100 to about 1:2; Element 11: admixing the purified pyrolysis oil with the hydrocarbon co-feed to yield a mixed feed; cracking the mixed feed in at least first and second steam cracker furnaces to yield a first product; and cracking a separate hydrocarbon feed stream to yield a second product. Element 12: wherein the hydrocarbon co-feed comprises at least one hydrocarbon selected from the group consisting of ethane, propane, butane, asphaltenes, resid, pitch, crude oil, naphtha, gas oil, liquefied petroleum gas, condensate, and combinations thereof; Element 13: removing oxygen-containing compounds from the recycle pyrolysis oil; Element 14: removing methanol from the recycle pyrolysis oil; Element 15: wherein the product comprises at least one hydrocarbon selected from the group consisting of an olefin, an aromatic, and combinations thereof; Element 16: wherein the recycle pyrolysis oil comprises about 95% by weight or greater of hydrocarbons having at least 5 carbon atoms, wherein the recycle pyrolysis oil comprises olefins in an amount of about 50% by weight or

- less, wherein the recycle pyrolysis oil comprises aromatic in an amount of about 20% by weight or less, and wherein the recycle pyrolysis oil has a final boiling point of about 400°C to about 600°C; Element 17: wherein the water has a pH of about 7 to about 9; Element 18: wherein the TAN of the purified pyrolysis oil is about 0.5 to about 1.5 mg KOG/g, as determined by ASTM
- 5 D664, wherein the total nitrogen content of the purified pyrolysis oil is about 400 wppm to about 850 wppm, and wherein the total chloride content of the purified pyrolysis oil is about 75 wppm to about 150 wppm; Element 19: wherein the recycle pyrolysis oil is at least partially derived from plastic waste; Element 20: wherein the recycle pyrolysis oil is at least partially derived from post-consumer use plastics. Element 21: wherein the recycle pyrolysis oil further
- 10 comprises at least one additional contaminant selected from the group consisting of fluorine, a fluorine containing compound, bromine, a bromine containing compound, phosphorous, a phosphorous containing compound, and combinations thereof, and wherein the method further comprises removing at least a portion of the at least one additional contaminant from the pyrolysis oil.
- 15 **[0051]** Another example embodiment of the present disclosure is a method including: removing nitrogen from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total nitrogen content of about 850 wppm or less; and cracking the purified pyrolysis oil to produce a product. This example embodiment may include one or more of the of the following: Element 1: contacting the recycle pyrolysis oil with water to yield the purified pyrolysis oil;
- 20 Element 2: cracking the purified pyrolysis oil to produce a product comprises steam cracking the purified pyrolysis oil in the presence of steam; Element 3: wherein cracking the purified pyrolysis oil is performed in the presence of a hydrocarbon co-feed; Element 4: admixing the purified pyrolysis oil with the co-feed to yield a mixed feed; and cracking the mixed feed; Element 5: wherein the cracking the mixed fixed is performed in a steam cracking furnace, and
- 25 wherein the method comprises cracking a second hydrocarbon feed in the steam cracking furnace, wherein the second hydrocarbon feed is segregated from the purified pyrolysis oil in the steam cracking furnace; Element 6: wherein the hydrocarbon co-feed is heavier than the second hydrocarbon feed that is segregated; Element 7: wherein the cracking the purified pyrolysis oil is performed in a steam cracking furnace, wherein the purified pyrolysis oil and
- 30 the hydrocarbon co-feed are separately fed to the steam cracking furnace; Element 8: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the hydrocarbon co-feed; Element 9: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the steam; Element 10: wherein the hydrocarbon co-feed and the purified pyrolysis oil are present in a purified pyrolysis oil to hydrocarbon co-feed weight ratio of about

1:100 to about 1:2; Element 11: admixing the purified pyrolysis oil with the hydrocarbon co-feed to yield a mixed feed; cracking the mixed feed in at least first and second steam cracker furnaces to yield a first product; and cracking a separate hydrocarbon feed stream to yield a second product. Element 12: wherein the hydrocarbon co-feed comprises at least one
5 hydrocarbon selected from the group consisting of ethane, propane, butane, asphaltenes, resid, pitch, crude oil, naphtha, gas oil, liquefied petroleum gas, condensate, and combinations thereof; Element 13: removing oxygen-containing compounds from the recycle pyrolysis oil; Element 14: removing methanol from the recycle pyrolysis oil; Element 15: wherein the product comprises at least one hydrocarbon selected from the group consisting of an olefin, an
10 aromatic, and combinations thereof; Element 16: wherein the recycle pyrolysis oil comprises about 95% by weight or greater of hydrocarbons having at least 5 carbon atoms, wherein the recycle pyrolysis oil comprises olefins in an amount of about 50% by weight or less, wherein the recycle pyrolysis oil comprises aromatic in an amount of about 20% by weight or less, and wherein the recycle pyrolysis oil has a final boiling point of about 400°C to about 600°C;
15 Element 17: wherein the water has a pH of about 7 to about 9; Element 18: wherein the TAN of the purified pyrolysis oil is about 0.5 to about 1.5 mg KOG/g, as determined by ASTM D664, wherein the total nitrogen content of the purified pyrolysis oil is about 400 wppm to about 850 wppm, and wherein the total chloride content of the purified pyrolysis oil is about 75 wppm to about 150 wppm; Element 19: wherein the recycle pyrolysis oil is at least partially
20 derived from plastic waste; Element 20: wherein the recycle pyrolysis oil is at least partially derived from post-consumer use plastics. Element 21: wherein the recycle pyrolysis oil further comprises at least one additional contaminant selected from the group consisting of fluorine, a fluorine containing compound, bromine, a bromine containing compound, phosphorous, a phosphorous containing compound, and combinations thereof, and wherein the method further
25 comprises removing at least a portion of the at least one additional contaminant from the pyrolysis oil.

[0052] Another example embodiment of the present disclosure is a method including: removing chlorides from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total chloride content of about 150 wppm or less. The method further may include cracking the
30 purified pyrolysis oil to produce a product. This example embodiment may include one or more of the of the following: Element 1: contacting the recycle pyrolysis oil with water to yield the purified pyrolysis oil; Element 2: cracking the purified pyrolysis oil to produce a product comprises steam cracking the purified pyrolysis oil in the presence of steam; Element 3: wherein cracking the purified pyrolysis oil is performed in the presence of a hydrocarbon co-

feed; Element 4: admixing the purified pyrolysis oil with the co-feed to yield a mixed feed; and cracking the mixed feed; Element 5: wherein the cracking the mixed feed is performed in a steam cracking furnace, and wherein the method comprises cracking a second hydrocarbon feed in the steam cracking furnace, wherein the second hydrocarbon feed is segregated from the purified pyrolysis oil in the steam cracking furnace; Element 6: wherein the hydrocarbon co-feed is heavier than the second hydrocarbon feed that is segregated; Element 7: wherein the cracking the purified pyrolysis oil is performed in a steam cracking furnace, wherein the purified pyrolysis oil and the hydrocarbon co-feed are separately fed to the steam cracking furnace; Element 8: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the hydrocarbon co-feed; Element 9: wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the steam; Element 10: wherein the hydrocarbon co-feed and the purified pyrolysis oil are present in a purified pyrolysis oil to hydrocarbon co-feed weight ratio of about 1:100 to about 1:2; Element 11: admixing the purified pyrolysis oil with the hydrocarbon co-feed to yield a mixed feed; cracking the mixed feed in at least first and second steam cracker furnaces to yield a first product; and cracking a separate hydrocarbon feed stream to yield a second product. Element 12: wherein the hydrocarbon co-feed comprises at least one hydrocarbon selected from the group consisting of ethane, propane, butane, asphaltenes, resid, pitch, crude oil, naphtha, gas oil, liquefied petroleum gas, condensate, and combinations thereof; Element 13: removing oxygen-containing compounds from the recycle pyrolysis oil; Element 14: removing methanol from the recycle pyrolysis oil; Element 15: wherein the product comprises at least one hydrocarbon selected from the group consisting of an olefin, an aromatic, and combinations thereof; Element 16: wherein the recycle pyrolysis oil comprises about 95% by weight or greater of hydrocarbons having at least 5 carbon atoms, wherein the recycle pyrolysis oil comprises olefins in an amount of about 50% by weight or less, wherein the recycle pyrolysis oil comprises aromatic in an amount of about 20% by weight or less, and wherein the recycle pyrolysis oil has a final boiling point of about 400°C to about 600°C; Element 17: wherein the water has a pH of about 7 to about 9; Element 18: wherein the TAN of the purified pyrolysis oil is about 0.5 to about 1.5 mg KOG/g, as determined by ASTM D664, wherein the total nitrogen content of the purified pyrolysis oil is about 400 wppm to about 850 wppm, and wherein the total chloride content of the purified pyrolysis oil is about 75 wppm to about 150 wppm; Element 19: wherein the recycle pyrolysis oil is at least partially derived from plastic waste; Element 20: wherein the recycle pyrolysis oil is at least partially derived from post-consumer use plastics. Element 21: wherein the recycle pyrolysis oil further comprises at least one additional contaminant selected from the group consisting of fluorine, a

fluorine containing compound, bromine, a bromine containing compound, phosphorous, a phosphorous containing compound, and combinations thereof, and wherein the method further comprises removing at least a portion of the at least one additional contaminant from the pyrolysis oil.

5 **EXAMPLES**

[0053] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the disclosure.

Example 1

- 10 [0054] This example is provided to illustrate removal of contaminants from a recycle pyrolysis oil with a water wash. The water used in this example was deionized water. The recycle pyrolysis oil was at least partially derived from plastic waste and had the following properties: specific gravity between 0.78 and 0.8, kinematic viscosity between 1.2 cSt and 2 cSt, and boiling range of about 90°F to about 875°F (as determined in accordance with ASTM
15 2887). The recycle pyrolysis oil and the water were used in a 50:50 volume ratio. Each wash cycle included combining the recycle pyrolysis oil and the water in a shaker followed by agitation for 5-10 minutes and then centrifugal separation. This was repeated with new deionized water for a total of 4 wash cycles with the total nitrogen content and total acid number (TAN) of the recycle pyrolysis oil recorded initially and then after each wash cycle. The results
20 of this example are provided in the table below.

Table 1

					Wash Cycle			
		Method	Units	Prewash	1	2	3	4
Pyoil Sample 1	Total Nitrogen	ASTM D5762	wppm	1300	570	520	490	470
	TAN	ASTM D664	Mg KOH/g	2.16	1.3	1.15	1.05	1

Example 2

- [0055] This example is provided to further illustrate removal of contaminants from a recycle
25 pyrolysis oil with a water wash. The water used in this example was deionized water. The pH of the water was adjusted with sodium hydroxide to 9 and 12 for Samples 6 and 7, respectively. The recycle pyrolysis oil was at least partially derived from plastic waste and had the following

properties: specific gravity between 0.78 and 0.8, kinematic viscosity between 1.2 cSt and 2 cSt, and boiling range of about 90°F to about 875°F (as determined in accordance with ASTM 2887). The recycle pyrolysis oil and the water were used in a 50:50 volume ratio. A single wash cycle was performed that included combining the recycle pyrolysis oil and the water in a shaker
5 followed by agitation for 5-10 minutes and then centrifugal separation. The total nitrogen, basic nitrogen, non-basic nitrogen, and total chloride content was determined for the recycle pyrolysis oil both pre- and post-wash. The total nitrogen was determined in accordance with ASTM D5762. The basic nitrogen was determined in accordance with UOP 269. The non-basic nitrogen was determined by differential of the total and basis nitrogen. The total chlorides were
10 determined in accordance with ASTM 7359.

[0056] The results of the example are provided in the table below.

Table 2

Pyoil Sample	pH	Total Nitrogen			Basic Nitrogen			Non-Basic Nitrogen			Total Chloride		
		Pre- Wash (wppm)	Post- Wash (wppm)	% Removal	Pre- Wash (wppm)	Post- Wash (wppm)	% Removal	Pre- Wash (wppm)	Post- Wash (wppm)	% Removal	Pre- Wash (wppm)	Post- Wash (wppm)	% Removal
2	7	1366	840	39	444	262	41	922	578	37	--	--	--
3	7	1300	700	46	275	168	39	1025	532	48	178	90	49
4	7	1100	570	48	243	135	44	857	435	49	260	110	58
5	7	900	560	38	243	129	47	657	431	34	212	136	36
6	9	900	610	32	243	135	44	657	475	28	212	140	33
7	12	900	750	17	243	178	27	657	572	13	212	--	--

Example 3

- [0057] The following example is provided to further illustrate removal of contaminants from a recycle pyrolysis oil with a water wash. The water used in this example was deionized. The recycle pyrolysis oil was at least partially derived from plastic waste and had the following properties: specific gravity between 0.78 and 0.8, kinematic viscosity between 1.2 cSt and 2 cSt, and boiling range of about 90°F to about 875°F (as determined in accordance with ASTM 2887). The recycle pyrolysis oil and the water were used in a 50:50 volume ratio. Each wash cycle included combining the recycle pyrolysis oil and the water in a shaker followed by agitation for 5-10 minutes and then centrifugal separation. Samples 8-10 were not washed.
- Sample 11 was tested without washing and also with 6 wash cycles. Sample 12 was tested without washing and with 3 wash cycles. The samples (with or without washing) were then separately fed into a pilot scale steam cracking furnace unit. A gas chromatography system and method were used for measurement of the steam cracker furnace effluent to identify and quantify peaks for carbon monoxide (CO) and carbon dioxide (CO₂). The peak area for CO and CO₂ was then converted back into mass percent in the base feed via calculation. The carbon monoxide and carbon dioxide yields were reduced for the washed samples, indicating removal of oxygenates from the recycle pyrolysis oil from the washing step.

Table 3

	CO Yield (wt%)	CO ₂ Yield (wt%)
Sample 8	0.37	0.03
Sample 9	0.67	0.09
Sample 10	0.6	0.1
Sample 11	0.51	0.09
Sample 11 (washed)	0.26	0.05
Sample 12	0.56	0.03
Sample 12 (washed)	0.29	not detected

- [0058] While the disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the disclosure as disclosed herein. Although individual embodiments are discussed, the present disclosure covers all combinations of all those embodiments.
- [0059] While compositions, methods, and processes are described herein in terms of “comprising,” “containing,” “having,” or “including” various components or steps, the

compositions and methods can also “consist essentially of” or “consist of” the various components and steps. The phrases, unless otherwise specified, “consists essentially of” and “consisting essentially of” do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

5 [0060] All numerical values within the detailed description and the claims herein modified by “about” or “approximately” with respect the indicated value are intended to take into
10 account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0061] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other
15 lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited.

CLAIMS:

1. A method comprising:
contacting a recycle pyrolysis oil with water to produce a purified pyrolysis oil; and
cracking the purified pyrolysis oil to produce a product.
2. A method comprising:
reducing the total acid number of a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a TAN, as determined by ASTM D664, of about 1.5 mg KOH/g or less; and
cracking the purified pyrolysis oil to produce a product.
3. A method comprising:
removing nitrogen from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total nitrogen content of about 850 wppm or less; and
cracking the purified pyrolysis oil to produce a product.
4. A method comprising:
removing chlorides from a recycle pyrolysis oil to yield a purified pyrolysis oil comprising a total chloride content of about 150 wppm or less; and
cracking the purified pyrolysis oil to produce a product.
5. The method of any of claims 2 to 4, comprising contacting the recycle pyrolysis oil with water to yield the purified pyrolysis oil.
6. The method any of claims 1 to 5, wherein cracking the purified pyrolysis oil to produce a product comprises steam cracking the purified pyrolysis oil in the presence of steam.
7. The method of any of claims 1 to 6, wherein cracking the purified pyrolysis oil is performed in the presence of a hydrocarbon co-feed.
8. The method of claim 7, further comprising:
admixing the purified pyrolysis oil with the co-feed to yield a mixed feed; and
cracking the mixed feed.

9. The method of claim 8, wherein the cracking the mixed feed is performed in a steam cracking furnace, and wherein the method comprises cracking a second hydrocarbon feed in the steam cracking furnace, wherein the second hydrocarbon feed is segregated from the purified pyrolysis oil in the steam cracking furnace.
10. The method of claim 9, wherein the hydrocarbon co-feed is heavier than the second hydrocarbon feed that is segregated.
11. The method of claim 7, wherein the cracking the purified pyrolysis oil is performed in a steam cracking furnace, wherein the purified pyrolysis oil and the hydrocarbon co-feed are separately fed to the steam cracking furnace.
12. The method of claim 11, wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the hydrocarbon co-feed.
13. The method of claim 11, wherein the purified pyrolysis oil is fed to the steam cracking furnace downstream of the steam.
14. The method of claim 7, wherein the hydrocarbon co-feed and the purified pyrolysis oil are present in a purified pyrolysis oil to hydrocarbon co-feed weight ratio of about 1:100 to about 1:2.
15. The method of claim 7, further comprising:
admixing the purified pyrolysis oil with the hydrocarbon co-feed to yield a mixed feed;
cracking the mixed feed in at least first and second steam cracker furnaces to yield a first product; and
cracking a separate hydrocarbon feed stream to yield a second product.
16. The method of any of claims 6 to 15, wherein the hydrocarbon co-feed comprises at least one hydrocarbon selected from the group consisting of ethane, propane, butane, asphaltenes, resid, pitch, crude oil, naphtha, gas oil, liquefied petroleum gas, condensate, and combinations thereof.

17. The method of any of claims 7 to 16, further comprising removing oxygen-containing compounds from the recycle pyrolysis oil.
18. The method of any of claims 1 to 17, further comprising removing methanol from the recycle pyrolysis oil.
19. The method of any of claims 1 to 18, wherein the recycle pyrolysis oil further comprises at least one additional contaminant selected from the group consisting of fluorine, a fluorine containing compound, bromine, a bromine containing compound, phosphorous, a phosphorous containing compound, and combinations thereof, and wherein the method further comprises removing at least a portion of the at least one additional contaminant from the pyrolysis oil.
20. The method of any of claims 1 to 19, wherein the product comprises at least one hydrocarbon selected from the group consisting of an olefin, an aromatic, and combinations thereof.
21. The method of any of claims 1 to 20, wherein the recycle pyrolysis oil comprises about 95% by weight or greater of hydrocarbons having at least 5 carbon atoms, wherein the recycle pyrolysis oil comprises olefins in an amount of about 50% by weight or less, wherein the recycle pyrolysis oil comprises aromatic in an amount of about 20% by weight or less, and wherein the recycle pyrolysis oil has a final boiling point of about 400°C to about 600°C.
22. The method of any of claims 1 and 5 to 21, wherein the water has a pH of about 7 to about 10.
23. The method of any of claims 1 to 22, wherein the TAN of the purified pyrolysis oil is about 0.5 to about 1.5 mg KOG/g, as determined by ASTM D664, wherein the total nitrogen content of the purified pyrolysis oil is about 400 wppm to about 850 wppm, and wherein the total chloride content of the purified pyrolysis oil is about 75 wppm to about 150 wppm.
24. The method of any of claims 1 to 23, wherein the recycle pyrolysis oil is at least partially derived from plastic waste.
25. The method of any of claims 1 to 24, wherein the recycle pyrolysis oil is at least partially derived from post-consumer use plastics.