Systems and methods for producing n-paraffins from low value feedstocks are provided. The method can include hydroprocessing at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydroprocessed kerosene product comprising n-paraffins. The n-paraffins can be separated from the hydroprocessed kerosene product to produce an n-paraffins product.
SYSTEMS AND METHODS FOR PRODUCING N-PARAFFINS FROM LOW VALUE FEEDSTOCKS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application having Ser. No. 61/113,935, filed on Nov. 12, 2008, which is incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] Embodiments of the present invention generally relate to systems and methods for producing normal paraffins or linear paraffins ("n-paraffins") from low value feedstocks. More particularly, embodiments of the present invention relate to systems and methods for producing n-paraffins from a kerosene fraction recovered from a thermally cracked hydrocarbon.

[0004] 2. Description of the Related Art

[0005] N-paraffins are traditionally produced from a high quality kerosene fraction of crude oil that is recovered from an atmospheric distillation unit ("ADU"). Such kerosene fraction is referred to as "straight-run kerosene." The n-paraffins product separated from straight-run kerosene is often converted to linear alkyl benzenes ("LAB") and used in the production of detergents. Other uses of n-paraffins include chlorinated paraffins and secondary alkane sulfonates ("SAS"). The n-paraffins product can also be further purified and processed for use in higher quality products, such as cosmetics, food-grade products, and specialty lubricants.

[0006] Conventional n-paraffins production processes must meet strict processing conditions in order to separate the n-paraffins from the straight-run kerosene. One particular processing condition that must be met is the concentration level of impurities allowed in the kerosene fraction must be low in order to separate the n-paraffins therefrom. For example, nitrogen-containing compounds (an impurity) must be reduced to a concentration below 1 ppmw in order to meet the contaminant specifications of the process required to separate the n-paraffins from the straight-run kerosene. In order to reduce the amount of impurities to required levels, the straight-run kerosene frequently requires severe hydrotreating. Therefore, not only are n-paraffins produced from an expensive hydrocarbon feed, i.e. straight-run kerosene, the hydrotreating conditions require special equipment and is expensive to construct, operate, and maintain.

[0007] There is a need, therefore, for improved systems and methods for producing n-paraffins from low value feedstocks.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] So that the recited features of the present invention can be understood in detail, a more particular description of the invention may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0009] FIG. 1 depicts an illustrative n-paraffins production system, according to one or more embodiments described.

[0010] FIG. 2 depicts an illustrative n-paraffins recovery system, according to one or more embodiments described.

[0011] FIG. 3 depicts an illustrative n-paraffins purification system, according to one or more embodiments described.

DETAILED DESCRIPTION

[0012] A detailed description will now be provided. Each of the appended claims defines a separate invention, which for infringement purposes is recognized as including equivalents to the various elements or limitations specified in the claims. Depending on the context, all references below to the "invention" may in some cases refer to certain specific embodiments only. In other cases it will be recognized that references to the "invention" will refer to subject matter recited in one or more, but not necessarily all, of the claims. Each of the inventions will now be described in greater detail below, including specific embodiments, versions and examples, but the inventions are not limited to these embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the inventions, when the information in this patent is combined with publicly available information and technology.

[0013] Systems and methods for producing n-paraffins are provided. The method can include hydrotreating at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydrotreated kerosene product comprising n-paraffins. The n-paraffins can be separated from the hydrotreated kerosene product to produce an n-paraffins product.

[0014] FIG. 1 depicts an illustrative n-paraffins production system 100, according to one or more embodiments. The n-paraffins production system 100 can include, but is not limited to, one or more thermal cracking units 105, one or more hydrotreating units 115, one or more n-paraffins recovery units 120, and one or more n-paraffins purification units 130. A hydrocarbon feed via line 103 can be introduced to the thermal cracking unit 105 to produce one or more thermally cracked hydrocarbon products (three are shown 107, 109, and 111). The thermally cracked hydrocarbon products can include, but are not limited to, a light hydrocarbon fraction via line 107, a heavy hydrocarbon fraction via line 109, and a kerosene fraction via line 111. In one or more embodiments, at least a portion of the kerosene fraction via line 111 and a hydrogen containing feed via line 113 can be introduced to the hydrotreating unit 115 to produce an overhead or off gas via line 117 and a hydrotreated kerosene product via line 119. The hydrotreating unit 115 can convert olefins to n-paraffins and/or reduce the concentration of sulfur, nitrogen, and/or oxygen-containing compounds and other impurities contained in the kerosene fraction in line 111. As such, the hydrotreated kerosene in line 119 can have a reduced concentration of impurities, such as sulfur and nitrogen-containing compounds, and an increased amount of n-paraffins relative to the kerosene fraction in line 111. The hydrotreated kerosene via line 119 can be introduced to the n-paraffins recovery unit 120 to provide a kerosene raffinate via line 121 and an n-paraffins product via line 123.

[0015] The hydrocarbon feed in line 103 can include any hydrocarbon or combination of hydrocarbons containing n-paraffins. For example, the hydrocarbon feed in line 103 can include one or more heavy and/or low value hydrocarbons. Illustrative hydrocarbon feeds in line 103 can include, but are not limited to, residues from the atmospheric and/or vacuum distillation of petroleum crudes, crude oils, heavy
In one or more embodiments, a second hydrocarbon feed via line 106 can be introduced to the hydrocarbon feed in line 103, the kerosene fraction in line 111, and/or the hydrotreated kerosene in line 119. The second hydrocarbon feed in line 106 can include straight-run kerosene provided from an atmospheric distillation unit, for example. In another embodiment, the second hydrocarbon feed in line 106 can include n-paraffins having from 8 to 20 carbon atoms. The second hydrocarbon feed in line 106 can have a concentration of n-paraffins having from 10 to 14 carbon atoms ranging from a low of about 10 wt %, about 15 wt %, or about 20 wt % to a high of about 30 wt %, about 35 wt %, or about 40 wt %.

The hydrocarbon feed in line 106 can have a concentration of sulfur-containing compounds ranging from a low of about 50 ppmw, about 60 ppmw, or about 80 ppmw to a high of about 115 ppmw, about 130 ppmw, or about 150 ppmw. The second hydrocarbon feed in line 106 can have a concentration of nitrogen-containing compounds ranging from a low of about 1 ppmw, about 2 ppmw, or about 3 ppmw to a high of about 5 ppmw, about 10 ppmw, or about 15 ppmw.

The composition or make-up of the hydrocarbon feed in line 103, with or without addition of the second hydrocarbon in line 106, can include, but is not limited to, paraffins, olefins, aromatics, and one or more impurities, such as sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, heavy metals, e.g. nickel and vanadium, and the like. The hydrocarbon feed in line 103 can have a concentration of paraffins ranging from a low of about 5 wt % to a high of about 90 wt %. The hydrocarbon feed in line 103 can have a concentration of n-paraffins having from 10 to 14 carbon atoms ranging from a low of about 5 wt %, about 10 wt %, or about 15 wt % to a high of about 25 wt %, about 30 wt %, or about 35 wt %. The hydrocarbon feed in line 103 can have a concentration of olefins ranging from a low of about 5 wt %, about 10 wt %, or about 15 wt % to a high of about 20 wt %, about 25 wt %, or about 30 wt %.

The aromatics can include, but are not limited to, monocyclic aromatics, such as alkyl-substituted benzenes, tetralins, alkyl-substituted tetralins, indanes, and alkyl-substituted indanes; and bicyclic aromatics, such as naphthalenes, biphenyls, and acenaphthenes. The hydrocarbon feed in line 103 can have a concentration of aromatics ranging from a low of about 1 wt %, about 3 wt %, or about 5 wt % to a high of about 10 wt %, about 20 wt %, or about 30 wt %.

The sulfur-containing compounds can include, but are not limited to, mercaptans, sulfides, thiophenes, and combinations thereof. The hydrocarbon feed in line 103 can have a concentration of sulfur-containing compounds ranging from a low of about 2 ppmw, about 100 ppmw, or about 500 ppmw to a high of about 10,000 ppmw, about 20,000 ppmw, or about 30,000 ppmw. The nitrogen-containing compounds can include, but are not limited to, indoles, quinolines, pyridines, and combinations thereof. The hydrocarbon feed in line 103 can have a concentration of nitrogen-containing compounds ranging from a low of about 1 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 600 ppmw, about 700 ppmw, or about 800 ppmw. The oxygen-containing compounds, i.e. heteroatom containing compounds, can include, but are not limited to, phenolics. The hydrocarbon feed in line 103 can have a concentration of oxygen-containing compounds ranging from a low of about 10 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 1,000 ppmw, about 3,000 ppmw, or about 5,000 ppmw.

The second hydrocarbon in line 106, if added, can be mixed or blended with the hydrocarbon feed in line 103, the kerosene fraction in line 111, and/or the hydrotreated kerosene in line 119 in any desired amount or ratio. For example, the second hydrocarbon via line 106 can be introduced to the hydrotreated kerosene in line 119 to provide a hydrocarbon mixture having nitrogen-containing compounds ranging from a low of about 5 ppmw, about 10 ppmw, or about 15 ppmw to a high of about 60 ppmw, about 80 ppmw, or about 100 ppmw. As such, the volume or weight ratio of the second hydrocarbon in line 106 to the hydrotreated kerosene in line 119 can depend, at least in part, on the desired level or concentration of nitrogen-containing compounds. Other compounds that can be used to determine the amount of the second hydrocarbon in line 106 that can be introduced to the hydrotreated kerosene in line 119 include, but are not limited to, the concentration of sulfur-containing compounds, n-paraffins, oxygen-containing compounds, aromatics, and any combination thereof. Similarly, the amount of the second hydrocarbon introduced to the hydrocarbon feed in line 103 and/or the kerosene fraction in line 111 can depend, at least in part, on a desired level or concentration of one or more compounds for that particular feed in the n-paraffins production process 100.

In one or more embodiments, at least a portion of the kerosene fraction in line 111 can bypass the hydroprocessing unit 115 via line 112 and can be introduced to the hydrotreated kerosene in line 119 and/or directly to the n-paraffins recovery unit 120. For example, about 5 wt %, about 10 wt %, about 20 wt %, about 30 wt %, about 40 wt %, or about 50 wt % of the kerosene fraction in line 111 can bypass via line 112 the hydroprocessing unit 115 and can be introduced to the hydrotreated kerosene in line 119 or directly to the n-paraffins recovery unit 120. In one or more embodiments, the portion or amount of the kerosene fraction via line 112 that can bypass the hydroprocessing unit 115 can depend, at least in part, on the amount of straight-run kerosene in line 106 and/or the concentrations of impurities in the kerosene fraction in line 111 and/or the concentrations of impurities that can be present in the hydrotreated kerosene in line 119.

The thermal cracking process carried out in the one or more thermal crackers 105 can convert the hydrocarbon feed introduced via line 103 to coke and lighter hydrocarbons, which include the kerosene fraction recovered via line 111. The thermal cracking unit 105 can include any thermal cracker suitable for thermally cracking the hydrocarbon feed introduced via line 103. Illustrative thermal cracking units 105 can include, but are not limited to, cokers, visbreaker, or any other thermal crackers, and combinations thereof. Cokers can include delayed cokers, fluid cokers, and/or flexicokers. Visblackers can include coil or furnace visbreakers and/or soaker visbreakers.

The kerosene fraction recovered via line 111 from the thermal cracking unit 105, with or without addition of the second hydrocarbon in line 106, can contain a variety of different hydrocarbon compounds and impurities. For example, the kerosene fraction in line 111 can include, but is not limited to, paraffins, olefins, aromatics, and impurities such as sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, water, and combinations thereof. The kerosene fraction in line 111 can
include a mixture of hydrocarbons having from about 1 to about 80 carbon atoms. For example, the kerosene fraction in line 111 can include a mixture of hydrocarbons having from about 1 to about 50, about 1 to about 60, or about 1 to about 70 carbon atoms.

[0022] The kerosene fraction in line 111 can have a concentration of paraffins ranging from a low of 5 wt % to a high of about 30 wt %. The kerosene fraction in line 111 can have a concentration of n-paraffins having from 10 to 14 carbon atoms ranging from a low of about 5 wt %, about 7 wt %, or about 8 wt % to a high of about 15 wt %, about 20 wt %, or about 25 wt %. In at least one specific embodiment, the kerosene fraction in line 111 can have a concentration of n-paraffins having from 10 to 14 carbon atoms of about 10 wt %, about 11 wt %, about 12 wt %, about 13 wt %, or about 14 wt %. The kerosene fraction in line 111 can have a concentration of olefins ranging from a low of about 5 wt %, about 10 wt %, or about 15 wt % to a high of about 20 wt %, about 25 wt %, or about 30 wt %. The kerosene fraction in line 111 can have a concentration of aromatics ranging from a low of about 1 wt %, about 3 wt % or about 5 wt % to a high of about 10 wt %, about 20 wt % or about 30 wt %. The kerosene fraction in line 111 can have a concentration of sulfur-containing compounds ranging from a low of about 2 ppmw, about 100 ppmw, or about 500 ppmw to a high of about 10,000 ppmw, about 20,000 ppmw, or about 30,000 ppmw. The kerosene fraction in line 111 can have a concentration of nitrogen-containing compounds ranging from a low of about 1 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 600 ppmw, about 700 ppmw, or about 800 ppmw. The kerosene fraction in line 111 can have a concentration of oxygen-containing compounds ranging from a low of about 10 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 1,000 ppmw, about 3,000 ppmw, or about 5,000 ppmw. The kerosene fraction in line 111 can have a concentration of water ranging from a low of about 10 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 200 ppmw, about 300 ppmw, or about 400 ppmw.

[0023] In one or more embodiments, about 90 vol % of the kerosene fraction in line 111 can be distilled at a temperature of from about 205°C to about 300°C, as determined according to ASTM D-86. In one or more embodiments, about 10 vol % of the kerosene fraction in line 111 can be distilled or vaporized at a temperature of from about 155°C to about 165°C. In one or more embodiments, about 50 vol % of the kerosene fraction in line 111 can be distilled or vaporized at a temperature of from about 210°C to about 230°C. In one or more embodiments, about 90 vol % of the kerosene fraction in line 111 can be distilled or vaporized at a temperature of from about 255°C to about 275°C. The kerosene fraction in line 111 can have a bromine index ranging from about 5 to about 400, as measured according to ASTM D-1159. For example, the kerosene fraction in line 119 can have a bromine index ranging from a low of about 5, about 10, or about 15 to a high of about 50, about 100, or about 200. In at least one specific embodiment, the kerosene fraction in line 111 can have a bromine index of at least 20, at least 40, at least 60, at least 80, or at least 100.

[0024] The light hydrocarbon fraction via line 107 and the heavy hydrocarbon fraction via line 109 can be further processed, blended with other hydrocarbon feeds or hydrocarbon feedstocks, used as a source of fuel, or the like. For example, the light hydrocarbon fraction via line 107 can be separated to provide naphtha. The heavy hydrocarbon fraction via line 109 can be recycled to the hydrocarbon feed in line 103. In another example the heavy hydrocarbon fraction via line 109 can be separated to provide coke, bunker oil, fuel oil, heavy gas oil, and the like.

[0025] As discussed above, the kerosene fraction via line 111 can be introduced to the one or more hydrocarbon processing units 115 to provide the hydrotreated kerosene via line 119 and the off-gas via line 117. The one or more hydroprocessing units 115 can include any system, device, or combination of systems and/or devices suitable for reducing the sulfur and nitrogen concentration of the kerosene fraction introduced via line 111 by converting sulfur and sulfur compounds to hydrogen sulfide ("H2S") and nitrogen and nitrogen compounds to ammonia ("NH3"), for example. The hydroprocessing unit 115 include a hydrocracking unit, a hydrotreating unit, or a combination thereof. At least a portion of the converted sulfur and nitrogen compounds and other impurities, such as converted oxygen-containing compounds, hydrogen, and other light gases, can be removed as the off-gas via line 117. At least a portion of the olefins contained in the kerosene fraction introduced via line 111 can be converted to n-paraffins to produce a hydrotreated kerosene product via line 119 enriched in n-paraffins relative to the kerosene fraction in line 111. In one or more embodiments, the amount of olefins contained in the kerosene fraction in line 111 that can be converted to n-paraffins can range from a low of about 5% to a high of about 100 wt %.

[0026] The hydrotreated kerosene in line 119, with or without the addition of the second hydrocarbon in line 106, can include the following components and amounts thereof. The hydrotreated kerosene in line 119 can have a concentration of paraffins ranging from a low of about 5 wt % to a high of about 95 wt %. The concentration of n-paraffins having 10 to 14 carbon atoms in line 119 can range from a low of about 20 wt %, about 22 wt %, about 24 wt %, or about 26 wt % to a high of about 27 wt %, about 30 wt %, about 33 wt %, or about 35 wt %. In at least one specific embodiment, the concentration of n-paraffins having 10 to 14 carbon atoms in line 119 can be at least 25 wt %, at least 30 wt %, at least 35 wt %, or at least 40 wt %. The hydrotreated kerosene in line 119 can have a concentration of olefins ranging from a low of about 0 wt %, about 1 wt %, or about 3 wt % to a high of about 5 wt %, about 7 wt %, or about 10 wt %. The hydrotreated kerosene in line 119 can have a concentration of aromatics ranging from a low of about 1 wt % to a high of about 10 wt %. The hydrotreated kerosene in line 119 can have a concentration of sulfur-containing compounds ranging from a low of about 1 ppmw or less, about 5 ppmw, about 10 ppmw, about 20 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 250 ppmw, about 400 ppmw, or about 500 ppmw. In at least one specific embodiment, the concentration of sulfur-containing compounds in line 119 can be at least 1 ppmw, at least 2 ppmw, at least 3 ppmw, at least 5 ppmw, at least 10 ppmw, at least 15 ppmw, at least 20 ppmw, or at least 25 ppmw. In at least one specific embodiment, the concentration of sulfur-containing compounds in line 119 can be at least 30 ppmw, at least 40 ppmw, at least 50 ppmw, at least 100 ppmw, at least 200 ppmw, or at least 250 ppmw. The hydrotreated kerosene in line 119 can have a concentration of nitrogen-containing compounds ranging from a low of about 1 ppmw or less, about 5 ppmw, about 10 ppmw, or about 15 ppmw to a high of about 80 ppmw, about 150 ppmw, or about 200 ppmw. In at least one specific embodiment, the concentration of nitrogen-containing compounds in line 119 can be at least
1 ppmw, at least 2 ppmw, at least 3 ppmw, at least 5 ppmw, at least 10 ppmw, at least 15 ppmw, at least 20 ppmw, or at least 25 ppmw. In at least one specific embodiment, the concentration of nitrogen-containing compounds in line 119 can be at least 30 ppmw, at least 40 ppmw, at least 50 ppmw, or at least 55 ppmw. In one or more embodiments, the hydrotreated kerosene in line 119 can have a concentration of sulfur-containing compounds of from about 50 ppmw to about 400 ppmw and a concentration of nitrogen containing compound of from about 5 ppmw to about 80 ppmw. The concentration of oxygen-containing compounds in line 119 can range from a low of about 10 ppmw, about 30 ppmw, or about 50 ppmw to a high of about 200 ppmw, about 400 ppmw or about 600 ppmw. In at least one specific embodiment, the concentration of oxygen-containing compounds in line 119 can be at least 50 ppmw, at least 75 ppmw, at least 100 ppmw, or at least 125 ppmw. The hydrotreated kerosene in line 119 can have a concentration of water ranging from a low of about 0 ppmw, about 5 ppmw, about 10 ppmw, about 50 ppmw, or about 100 ppmw to a high of about 150 ppmw, about 175 ppmw, or about 200 ppmw. In at least one specific embodiment, the concentration of water in line 119 can be at least 10 ppmw, at least 25 ppmw, at least 50 ppmw, at least 100 ppmw, or at least 150 ppmw.

[0027] The hydrotreated kerosene in line 119 can have a bromine index ranging from about 4 to about 120. For example, the hydrotreated kerosene in line 119 can have a bromine index ranging from a low of about 10, about 25, or about 50 to a high of about 100, about 150, or about 175. In at least one specific embodiment, the hydrotreated kerosene in line 119 can have a bromine index of at least 10, or at least 15, or at least 20.

[0028] The hydrogen containing gas via line 113 introduced to the hydrotreatment unit 115 can contain about 50% vol H₂ or more, about 65% vol H₂ or more, about 75% vol H₂ or more, about 85% vol H₂ or more, or about 95% vol H₂ or more. The balance of the hydrogen containing feed in line 113 can include, but is not limited to, other components typically found in refinery hydrogen, such as nitrogen, methane, and argon. The hydrogen containing feed in line 113 can contain less than about 3% mol H₂S, less than about 1% mol H₂S, less than 0.1% mol H₂S, less than about 0.01% mol H₂S, or less.

[0029] The one or more hydrotreatment units 115 can include one or more catalyst beds in any arrangement, configuration and/or orientation. The one or more catalyst beds can include fixed beds, fluidized beds, ebullating beds, slurry beds, moving beds, bubbling beds, any other suitable type of catalyst bed, or combinations thereof. The hydrotreatment unit 115 can be configured vertically for upward or downward flow through the one or more catalyst beds, or horizontally for lateral flow through the one or more catalyst beds. The one or more catalyst beds can be axial beds, axial/axial beds, radial beds, or any combination thereof. The one or more catalyst beds can be cold gas quenched, inter-cooled using one or more exchangers, or a combination thereof to control or otherwise regulate the temperature of the one or more catalyst beds. In at least one specific embodiment, the hydrotreatment unit 115 can include a single hydrotreatment stage, i.e. a single catalyst bed.

[0030] In one or more embodiments, any suitable catalyst or combination of catalysts for converting sulfur and sulfur compounds to H₂S and nitrogen and nitrogen compounds to NH₃, for example. The catalyst can include, but is not limited to, any one or more Group VIII metals of the Periodic Table of Elements, such as cobalt, nickel, palladium, iron, derivatives thereof, or combinations thereof. The catalyst can be combined with one or more Group VIA, IA, IIA, and/or IB metals of the Periodic Table of Elements, such as molybdenum or tungsten, oxides thereof, or combinations thereof. The catalyst can be supported. Illustrative catalyst supports can include, but are not limited to, alumina, silica-alumina, titania-zirconia, and the like.

[0031] The operating temperature of the one or more hydrotreatment units 115 can range from a low of about 200° C., about 225° C., or about 250° C. to a high of about 375° C., about 450° C., or about 500° C. For example, the operating temperature of the one or more hydrotreatment units 115 can range from 200° C. to about 420° C. or about 260° C. to about 355° C. The operating pressure of the one or more hydrotreatment units 115 can range from a low of about 1,000 kPa, about 1,350 kPa, or about 1,450 kPa to a high of about 5,500 kPa, about 10,000 kPa, or about 13,500 kPa or more. For example, the operating pressure of the one or more hydrotreatment units 115 can range from about 3,000 kPa to about 8,000 kPa or about 1,350 kPa to about 5,550 kPa.

[0032] As discussed above, the hydrotreated kerosene via line 119 can be introduced to the one or more n-paraffins recovery units 120 to provide the kerosene raffinate via line 121 and one or more n-paraffins products via line 123. The one or more n-paraffins recovery units 120 can include any system, device, or combination of systems and/or devices suitable for separating at least a portion of the n-paraffins from the hydrotreated kerosene in line 119. For example, the n-paraffins recovery unit 120 can include an adsorption/desorption process that selectively adsorbs the n-paraffins from the hydrotreated kerosene in line 119. The adsorbed paraffins can then be desorbed to provide the n-paraffins product via line 123. Other suitable separation processes can include, but are not limited to, solvent extraction, distillation, or combinations thereof.

[0033] The n-paraffins product in line 123 can include one or more n-paraffins having from 6 to 30 carbon atoms. For example, the n-paraffins product in line 123 can contain one or more n-paraffins having from about 10 to about 14 carbon atoms or from about 10 to about 18 carbon atoms, or from about 8 to about 16 carbon atoms. The n-paraffins product in line 123 can have an n-paraffins concentration of about 90 wt % or more, about 95 wt % or more, or about 97 wt % or more. The n-paraffins product in line 123 can have an n-paraffins concentration of about 97.5 wt % or more, about 98.5 wt % or more, or about 99 wt % or more. The n-paraffins product in line 123 can have a concentration of n-paraffins having from 10 to 14 carbon atoms of about 97 wt %, about 98 wt %, or about 99 wt % or more. The balance of the n-paraffins product in line 123 can include various hydrocarbons, such as aromatic hydrocarbons, non-n-paraffins hydrocarbons having a range of compounds with varying numbers of carbon atoms, sulfur-containing compounds, nitrogen-containing compounds, and any combination thereof. The n-paraffins product in line 123 can have a concentration of aromatic hydrocarbons ranging from a low of about 100 ppmw, about 250 ppmw, or about 500 ppmw to a high of about 5,000 ppmw, about 10,000 ppmw, or about 20,000 ppmw. The n-paraffins product in line 123 can have a concentration of sulfur or sulfur-containing compounds of less than about 15 ppmw, less than about 10 ppmw, or less than about 5 ppmw. The n-paraffins product in line 123 can have a concentration of nitrogen or nitrogen-containing compounds of less than about
15 ppmw, less than about 10 ppmw, or less than about 5 ppmw. The paraffin product in line 123 can have a bromine index ranging from a low of about 1, about 3, or about 6 to a high of about 10, about 12, or about 15. The paraffin product in line 123 can have a bromine index of less than about 25, less than about 20, less than about 15, or less than about 10.

[0034] The n-paraffins product in line 123 can be sold as a final n-paraffins product, further processed to provide a purified n-paraffins product, and/or used in the production of one or more products that requires n-paraffins. The purified n-paraffins product in line 123 can be distilled to obtain various fractions of n-paraffins, and blends thereof, containing various ranges of carbon numbers and respective molecular weights for the desired product applications. In at least one specific embodiment, the n-paraffins product in line 123 can be processed to provide linear alkyl benzene (“LAB”). For example, the n-paraffins can be passed through a catalytic dehydrogenation zone where some of the n-paraffins can be converted to olefins. The n-paraffins and olefin mixture can then be introduced to an alkylation zone where the olefins react with the aromatic substrate to produce linear alkyl benzenes. The linear alkylbenzenes can then be converted to linear alkylsulfonate (“LAS”) by sulfonation. The linear alkylbenzenes can also be used to produce a variety of anionic surfactants compounded into detergents, cleaning compounds, bar soaps and laundry or dishwashing detergents.

[0035] A “high quality” or first purified n-paraffins product can be produced by introducing at least a portion of the n-paraffins product in line 123 to the one or more n-paraffins purification units 130 via line 125. The n-paraffins purification unit 130 can provide one or more purified n-paraffins products (two are shown, 131, 133). The n-paraffins purification unit 130 can include, for example, a hydroprocessing unit which can hydrotreat or “hydro-polish” the n-paraffins product to provide a first purified n-paraffins product via line 131 having a reduced concentration sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, and/or olefins that can be present in the n-paraffins product in line 123. The hydroprocessing unit can be similar to the hydroprocessing unit 115 discussed and described above.

[0036] The first purified n-paraffins product in line 131 can have a concentration of aromatic hydrocarbons ranging from a low of about 25 ppmw, about 100 ppmw, about 250 ppmw, or about 500 ppmw to a high of about 3,000 ppmw, about 4,500 ppmw, or about 6,000 ppmw. For example, the concentration of aromatic hydrocarbons in the first purified n-paraffins product in line 131 can be less than about 5,000 ppmw. The n-paraffins product in line 123 can have a concentration of sulfur or sulfur-containing compounds of less than about 10 ppmw, less than about 5 ppmw, or less than about 2 ppmw. The n-paraffins product in line 123 can have a concentration of nitrogen or nitrogen-containing compounds of less than about 10 ppmw, less than about 7 ppmw, or less than about 5 ppmw. The paraffin product in line 123 can have a bromine index ranging from a low of about 0.5, about 2, or about 3 to a high of about 5, about 7, or about 12.

[0037] An even “higher quality” or second purified n-paraffins product line 133 can be provided by further purifying the n-paraffins product introduced via line 125 to the n-paraffins purification unit 130. For example, the n-paraffins product in line 125 or the first purified n-paraffins product can undergo further purification to remove at least a portion of the aromatic compounds contained in the n-paraffins product in line 125 or the first purified n-paraffins product to produce the second purified n-paraffins via line 133. The second purified n-paraffins product in line 133 can have an n-paraffins concentration of about 99.1 wt % or more, about 99.3 wt % or more, or about 99.5 wt % or more. The concentration of the aromatic hydrocarbons in line 133 can range from a low of about 0 ppmw, about 5 ppmw, about 10 ppmw, about 15 ppmw, about 20 ppmw, or about 25 ppmw to a high of about 75 ppmw, about 100 ppmw, about 150 ppmw, or about 200 ppmw. The concentration of sulfur or sulfur-containing compounds in line 133 can be less than about 3 ppmw, less than about 1 ppmw, less than about 0.5 ppmw, or less than about 0.1 ppmw. The n-paraffins product in line 133 can have a bromine index of less than about 7, less than about 5, less than about 3, or less than about 2.

[0038] Any suitable separation/removal process can be used to reduce the amount of aromatics in the second purified n-paraffins product in line 133 relative to the n-paraffins product in line 125 and the first purified n-paraffins product. For example, an adsorption/desorption process can be used to separate the aromatic compounds from the n-paraffins product in line 125. Other suitable separation processes can include, but are not limited to, solvent extraction, adsorption/desorption, hydrogenation, sulfuric acid treating, distillation, and combinations thereof.

[0039] Referring again to the one or more thermal crackers 105, depending on the particular type of thermal cracker, the hydrocarbon feed in line 103 can be heated to a temperature ranging from a low of about 400°C to a high of about 900°C, and a pressure ranging from a low of about 100 kPa to a high of about 6,500 kPa to produce lighter components which can be recovered as a vapor and coke which forms as a solid residue in the coking unit. In a delayed coking process, the hydrocarbon feed via line 103 can be introduced to a coking drum, heated, and held at a temperature of from about 400°C to about 500°C. And a pressure of from about 300 kPa to about 900 kPa, for example, to deposit solid coke, while cracked vapors are taken overhead. Coke produced in the thermal cracking process can be transported to a storage area, used as a solid fuel, or the like. The cracked vapors can be introduced to one or more separators to provide the light hydrocarbon fraction via line 107, the heavy hydrocarbon fraction via line 109, and the kerosene fraction via line 111.

[0040] In a flexicoking process, the hydrocarbon feed via line 103 can circulate between a reactor and a heater. More specifically, the hydrocarbon feed via line 103 can be introduced into a fluidized bed, along with a stream of hot recirculating material. The fluidized bed can be at a pressure of from about 100 kPa to about 300 kPa and at a temperature of from about 480°C to about 590°C, for example. From the fluidized bed, a coke containing product can be circulated to a heater vessel, where it is heated. The heated coke can be introduced from the heater to a gasifier, where it reacts with air and steam. A gasifier product gas, referred to as coke gas and containing entrained coke particles can be returned to the heater and cooled by cold coke from the reactor to provide a portion of the reactor heat requirement. The recycle of the coke gas from the gasifier to the heater can provide the remainder of the heat requirement. Hot coke gas leaving the heater can be used to generate high-pressure steam before being processed for cleanup. The coke gas can be introduced to one or more separators to provide the light hydrocarbon fraction via line 107, the heavy hydrocarbon fraction via line 109, and the kerosene fraction via line 111.
In a fluid coking process, a fluidized bed reactor can be used in conjunction with a burner to produce coke and lighter hydrocarbons. The hydrocarbon feed via line 103 can be introduced to a scrubber, where heat can be exchanged with a reactor overhead effluent and the heaviest fraction of the hydrocarbons leaving the top of the reactor can be condensed. The total reactor feed, including both the fresh feed via line 103 and a recycle feed condensed in the scrubber, can be injected into a fluidized bed of coke in the reactor. The reactor feed can be at a pressure of from about 100 kPa to about 300 kPa and can be heated to a temperature of from about 700°C to about 950°C, for example. The coke can be deposited on fluidized coke particles, while the hydrocarbon vapors pass overhead into the scrubber. The reactor overhead can be scrubbed for solids removal and the high boiling material can be condensed and recycled to the reactor. The lighter hydrocarbons can be sent from the scrubber to one or more separators to provide the light hydrocarbon fraction via line 107, the heavy hydrocarbon fraction via line 109, and the kerosene fraction via line 111. Heat required to maintain the fluid coker at coking temperature can be supplied by circulating coke between the reactor and the burner. A portion of the coke produced in the reactor can be burned with air to provide the process heat requirements. Excess coke can be withdrawn from the burner and sent to storage, used as fuel in another process, or the like. The thermal cracking step of fluid-cokers and flexicokers can be similar. However, fluid-coking does not utilize the residual coke produced with the coker distillate while flexicoking employs the coke by-product for the production of low thermal value gas. Flexicokers and fluid-cokers can be as described and described in U.S. Pat. Nos. 2,813,916; 2,905,629; 2,905,733; 3,661,543; 3,816,084; 4,055,484 and 4,497,705, which are incorporated by reference herein.

The term coil (or furnace) visbreaking can refer to thermal cracking units where the cracking process occurs in the furnace tubes (or “coils”). The hydrocarbon feed via line 103 introduced to a coil visbreaker can be at a pressure of from about 150 kPa to about 1,000 kPa and heated to a temperature of from about 425°C to about 540°C, for example. The thermally cracked hydrocarbons exiting the furnace can be quenched until the cracking reactions. Quenching the cracked hydrocarbons exiting the furnace can include exchanging heat with the hydrocarbon feed in line 103 introduced to the furnace. In another example, a heat transfer medium, such as gas oil, can be used to quench the material exiting the furnace. The level or amount the hydrocarbon feed in line 103 cracks can be controlled by regulating the speed of flow of the hydrocarbon feed through the furnace tubes. The quenched cracked hydrocarbon product can then be introduced to one or more separators to provide the light hydrocarbon fraction via line 107, the heavy hydrocarbon fraction via line 109, and the kerosene fraction via line 111.

In a soaker visbreaker the majority of the cracking reactions can occur in a drum (the soaker) located after the furnace. The hydrocarbon feed introduced via line 103 can be at a pressure of from about 200 kPa to about 6,500 kPa and heated to a temperature and held (soaked) of from about 400°C to about 650°C, for example. Soaking the heated hydrocarbon feed for a predetermined period of time allows the cracking reactions to occur. The heated hydrocarbon feed can be soaked for a time period ranging from about 5 minutes to about 60 minutes. After the desired period of time, the cracked hydrocarbon product can be quenched. The quenched cracked hydrocarbon product can then be introduced to one or more separators to provide the light hydrocarbon fraction via line 107, the heavy hydrocarbon fraction via line 109, and the kerosene fraction via line 111. Lower temperatures can be used in soaker visbreaking as compared to coil visbreaking because the soaker visbreaker maintains the hydrocarbons at an elevated temperature for a comparatively longer duration than the coil visbreaking.

When a plurality of thermal crackers are used, those thermal crackers can be arranged in series, parallel, or a combination of series and parallel. For example, a first thermal cracker can provide a first thermally cracked hydrocarbon which can be introduced to a second thermal cracker to produce a second thermally cracked hydrocarbon. In another example, two thermal crackers, either the same or different, can crack two hydrocarbon feeds in parallel, with the cracked hydrocarbons combined thereafter to provide the thermally cracked hydrocarbon.

The one or more separators within the thermal cracking unit 105 can include any separator suitable for separating two or more hydrocarbon fractions from the thermally cracked hydrocarbon product. The separator can include any system, device, or combination of systems and/or devices that can provide kerosene via line 111, for example, splitting, distillation, and/or fractionation. In one or more embodiments, one or more packing materials, baffles, trays, plates, distributors, structured packed beds, random packed beds, collectors, and/or empty spaces can be disposed within the separator in any order, frequency, or configuration. In one or more embodiments, the separator can be an open column without internals.

FIG. 2 depicts an illustrative n-paraffins recovery unit 200, according to one or more embodiments. The n-paraffins recovery unit 200 can include one or more heaters 205, one or more adsorption/desorption units (two are shown, 225, 230), one or more compressors 240, and one or more separators (two are shown 250, 260). The first and second separation units 225, 230 can each include one or more adsorption/desorption beds (one is shown 226, 231, respectively). The hydroprocessed kerosene in line 119 can be introduced to the heater 205 to provide a heated kerosene via line 207. The kerosene can be heated to a temperature ranging from a low of about 90°C to a high of about 275°C. The heater 205 can be or include a direct fired heater, a heat exchanger within which heat is transferred from a heat transfer medium to the hydroprocessed kerosene, or the like.

As illustrated, the n-paraffins recovery unit 200 includes two adsorption/desorption units 225, 230, which can alternately be used to separate, i.e., adsorb and desorb n-paraffins from the heated kerosene in line 207. For example, the heated kerosene in line 207 can be introduced via line 208 to the first adsorption/desorption unit 225, which can adsorb at least a portion of the n-paraffins contained therein and an n-paraffins-lean hydrocarbon can be recovered via line 232. Once the adsorption/desorption bed 226 has adsorbed a sufficient amount of n-paraffins or has become saturated with n-paraffins, the heated kerosene introduced via line 208 can be stopped and redirected via line 209 to the second adsorption/desorption unit 230, which can adsorb at least a portion of the n-paraffins to provide a n-paraffins-lean hydrocarbon via line 233. A displacing medium or desorbent, line 212 provided from a compressed displacing medium in line 211 can be introduced to the first adsorption/desorption unit 225, which can displace at least a portion of the adsorbed n-paral-
fins to provide an n-paraffins-rich hydrocarbon via line 227. Once the n-paraffins have been displaced from the adsorption/desorption bed 226, the introduction of the displacing medium via line 212 can be stopped. Once the adsorption/desorption bed 231 has adsorbed a sufficient amount of n-paraffins or has become saturated with n-paraffins, the heated kerosene introduced via line 209 can be stopped and redirected via line 208 to the adsorption/desorption unit 225, and provided the adsorbed n-paraffins have been desorbed and recovered via line 227, which can again adsorb at least a portion of the n-paraffins to provide the n-paraffins-rich hydrocarbon via line 233. The displacing medium can be recovered by heating at a temperature of from about 250° C. to about 500° C., for example. A displacing medium or desorbent via line 213 provided from the compressed displacing medium in line 211 can be introduced to the second adsorption/desorption unit 230, which can displace a portion of the adsorbed n-paraffins to provide an n-paraffins-rich hydrocarbon via line 228. As such, the two adsorption/desorption units 225, 230 can be alternately operated such that the first adsorption/desorption unit 225 adsorbs n-paraffins while the second adsorption/desorption unit 230 desorbs n-paraffins and vice versa.

[0048] As shown, the heated kerosene via lines 208, 209 and the displacing medium via lines 212, and 213 are introduced to opposing ends of the adsorption/desorption units 225, 230. As such, the adsorption and desorption steps can be conducted counter-currently with respect to one another. For vertically oriented adsorption/desorption units 225, 230 the heated kerosene via lines 208, 209 can be introduced to the adsorption/desorption units 225, 230, respectively, such that the heated kerosene flows downwardly therethrough. The displacing medium via lines 212, 213 can be introduced to the adsorption/desorption units 225, 230, respectively, such that the displacing medium flows upwardly therethrough. In another example the co-current flow directions of the heated kerosene and the displacing medium can be reversed. Although not shown, the adsorption and desorption steps can be conducted co-currently with respect one another.

[0049] The n-paraffins-rich hydrocarbons via lines 227, 228 can be introduced to the separator 250 via line 229 and the n-paraffins-lean hydrocarbons via lines 232, 233 can be introduced to the separator 260 via line 234. The separator 250 can provide the n-paraffins product via line 123 and a recycle displacing medium via line 254 and the separator 260 can provide the kerosene raffinate via line 121 and a recycle displacing medium via line 264. The recycle displacing mediums via lines 264, 254 can be introduced to the compressor 240 to provide the compressed displacing mediums via line 211. The separators 250, 260 can separate the displacing medium from the n-paraffins-rich hydrocarbons and the n-paraffins-lean hydrocarbons using any suitable method. For example, the separators 250 can condense the n-paraffinic hydrocarbons and recover the condensed n-paraffins-rich hydrocarbons via line 123 and a gaseous displacing medium via line 254. Similarly, the separator 260 can condense the hydrocarbons in the n-paraffins-lean hydrocarbons introduced via line 234 to provide a condensed n-paraffins-lean hydrocarbon via line 121 and a gaseous displacing medium via line 264.

[0050] The displacing medium introduced to the first and second adsorption/desorption units 225, 230 can include any material capable of displacing the adsorbed n-paraffins. Suitable displacing mediums can include a polar material or a material with substantial polarizability compared to the normal n-paraffins. In one or more embodiments, the displacing medium can be represented by the general formula:

\[
R \rightarrow N \rightarrow R'
\]

[0051] where R, R', and R" are each selected from the group consisting of hydrogen and C_5 to C_13 alkyl radicals. For example, the displacing medium can include ammonia ("NH_3") and C_5 to C_13 primary, secondary, and tertiary amines. Other suitable displacing mediums can include, but are not limited to, hydrogen, sulfur dioxide ("SO_2"), C_5 to C_13 alcohols, C_5 to C_8 alkanes, glycols, halogenated compounds such as methyl and ethyl chloride and methyl fluoride, nitrated compounds such as nitro methane, and carbon dioxide ("CO_2"). In one or more embodiments, a fresh or make-up displacing medium can be introduced to the n-paraffins recovery unit via line 256. The displacing medium can be compressed and circulated via the compressor 240 within the n-paraffins recovery unit 200 or the circuit can be accomplished via an external source by integrating the system with the fresh or makeup line 256 and a suitable provision to reject or return the lower pressure displacing medium from line 254.

[0052] The adsorption/desorption beds 226, 231 can include any suitable medium capable of adsorbing n-paraffins while allowing at least a majority of the non n-paraffinic hydrocarbons, e.g., branched and cyclic hydrocarbons, to pass through the adsorption/desorption units 225, 230. For example, the adsorption/desorption beds 226, 231 can include molecular sieves. Illustrative molecular sieves can include crystalline zeolites containing an alkali or alkali earth metal, aluminum, silicon and/or oxygen. The molecular sieves can be, natural or synthetic and can have uniform pore spaces of from about 3 to about 15 Ångstroms ("Å"), depending upon the composition and conditions under which the molecular sieves were prepared. Molecular sieves having a pore size of about 5 Å can separate the normal n-paraffins from branched chain and cyclic compounds. Natural zeolites, having suitable molecular sieve properties, can include analcrite, NaAlS_i_2O_5.H_2O, and chabasite, CaAl_2Si_2O_7.6H_2O. Other naturally occurring material suitable for use as molecular sieves can be as discussed and described in the article “Molecular Sieve Action of Solids,” Quarterly Reviews, vol. III, p. 293-330 (1949), published by the Chemical Society (London). Synthetic zeolites having similar properties can be as described and described in U.S. Pat. No. 2,306,610, where a material of the formula (CaN_2)_2Al_2Si_4O_12.2H_2O is described, and in U.S. Pat. No. 2,522,426, where a material of the formula 4CaO.Al_2O_3.4SiO_2 is described. Other suitable molecular sieves can be as discussed and described in an article by Breek et al., which was published in the Journal of the American Chemical Society, Volume 78, page 593 et seq., in December 1956.

[0053] The adsorption and desorption of the n-paraffins within the adsorption/desorption units 225, 230 can be performed in a liquid and/or vapor phase. The adsorption and desorption of the n-paraffins in the adsorption/desorption units 225, 230 can be carried out at a temperature ranging from a low of about 95° C., about 200° C., or about 260° C. to a high of about 370° C., about 425° C. or about 485° C. For
example, the adsorption of the n-paraffins can be carried out in the vapor phase at a temperature of from about 95°C to about 300°C with the heated kerosene via lines 208, 209 at a partial pressure low enough to prevent an undesirable amount of condensation in the adsorption beds 226, 231. The partial pressure of the heated kerosene introduced via lines 208, 209 can be about 0.01 to about 0.7 of the pressure that would condense a hydrocarbon having a boiling point equal to the average boiling point of the heated kerosene at the temperature of operation. The desorption of the n-paraffins can be carried out at a temperature of from about 315°C to about 485°C and a pressure of from about 1.3 kPa to about 1.5 kPa with a sufficient amount of displacing agent introduced via lines 212, 213 to displace at least a portion of the adsorbed n-paraffins. Further adsorption and desorption process conditions and can be as discussed and described in U.S. Pat. Nos. 2,899,379; 3,248,322; 3,378,486; and 3,418,235. 

[0054] Although not shown, the purity of the n-paraffins-rich hydrocarbons via lines 227, 228 can be increased by pressurizing and then depressurizing the adsorption/desorption units 225, 230 after adsorption of the n-paraffins and prior to the desorption of the n-paraffins. For example, after the adsorption/desorption beds 226, 231 have adsorbed the desired amount of n-paraffins, the heated hydrocarbons via lines 208, 209 can be stopped and the pressure within the adsorption/desorption units 225, 230 can be allowed to increase to about 101% to about 500% of the adsorption pressure. The adsorption/desorption units 225, 230 can then be depressurized. The material that exists the adsorption/desorption beds 225, 231 during the depressurization and pressurization includes a major portion of n-paraffins, e.g. non n-paraffinic compounds, which can be adsorbed or desorbed within the adsorption/separation beds 226, 231. Although not shown, the purity of the n-paraffins-rich hydrocarbons via lines 227, 228 can also be increased through a temperature swing, e.g. increasing and then decreasing the temperature of the adsorption/desorption units 225, 230 after adsorption of the n-paraffins and prior to the desorption of the n-paraffins. 

[0055] The compressor 240 can include any device suitable for compressing a gas, and/or multi-phase fluid, for example one or more reciprocating, rotary, axial flow, centrifugal, diagonal or mixed-flow, scroll, or diaphragm compressors or any series and/or parallel combination thereof. The compressor 240 can have one or more compressor stages with or without intercooling between successive stages. In one or more embodiments, the pressure of the compressed displacing medium in line 211 can range from about 101 kPa to about 5,000 kPa.

[0056] FIG. 3 depicts an illustrative n-paraffins purification system 300, according to one or more embodiments. The n-paraffins purification system 300 can include one or more hydroprocessing or “hydro-polishing” units 305, one or more adsorption/desorption units 320, 325, and one or more separators 340, 350. The adsorption/desorption units 320, 325 can include one or more adsorption/desorption beds (one is shown 321, 326, respectively).

[0057] In one or more embodiments, the n-paraffins product in line 125 and a hydrogen containing gas via line 302 can be introduced to the hydroprocessing unit 305 to further remove at least a portion of any impurities that remain therein to provide a first purified n-paraffins product via line 307. The hydroprocessing unit 305 can be similar to the hydroprocessing unit 115 discussed and described above with reference to FIG. 1. The hydroprocessing unit 305 can act as a “guard” bed to remove or reduce the amount of impurities, such as sulfur-containing and nitrogen-containing compounds. As such, in addition to the first purified n-paraffins product via line 307, an off-gas via line 306 can also be recovered from the hydroprocessing unit 305. The off-gas can contain at least a portion of the impurities converted within the hydroprocessing unit 305. In at least one specific embodiment, all or a portion of the first purified n-paraffins product in line 307 can be recovered as the purified n-paraffins or “LP quality” n-paraffins product via line 313. At least one other specific embodiment, all or a portion of the first purified n-paraffins product in line 307 can be further processed via line 309 to provide the second purified n-paraffins via line 313. 

[0058] As illustrated, the n-paraffins purification unit 300 includes two adsorption/desorption units 320, 325, which can alternately be used to separate, i.e. adsorb and desorb impurities from the first purified n-paraffins in line 309. For example, the first purified n-paraffins in line 309 can be introduced via line 311 to the first adsorption/desorption unit 320, which can adsorb at least a portion of the impurities contained therein and a second purified n-paraffins product can be recovered via line 327. Once the adsorption/desorption bed 321 has adsorbed a sufficient amount of impurities or has become saturated with impurities, the first purified n-paraffins introduced via line 311 can be stopped and redirected via line 313 to the second adsorption/desorption unit 325, which can adsorb at least a portion of the impurities to provide a second purified n-paraffins product via line 328. A displacing medium or desorbent via line 361 can be introduced to the first adsorption/desorption unit 320, which can displace at least a portion of the adsorbed impurities to provide a second purified n-paraffins product via line 328. As such, the two adsorption/desorption units 320, 325 can be alternately operated such that the first adsorption/desorption unit 225 adsorbs n-paraffins while the second adsorption/desorption unit 320 adsorbs n-paraffins and vice versa. 

[0059] The first purified n-paraffins via lines 311, 313 and the displacing mediums via lines 361, 362 can be introduced to the same end or different ends (not shown) of the adsorption/separation units 320, 325. As shown, the first purified n-paraffins via lines 311, 313 and the displacing mediums via lines 361, 362 can be introduced to the same end of each adsorption/separation unit 320, 325. As such, the adsorption and desorption steps can be conducted co-currently with respect to one another. Although not shown, the first purified n-paraffins product via lines 311, 313 and the displacing mediums via lines 361, 362 can be introduced to opposing ends of the adsorption/desorption units 320, 325. As such, the adsorption and desorption steps can be conducted counter-
currently with respect to one another. For example, for vertically oriented adsorption/desorption units 320, 325 the first purified n-paraffins product via lines 311, 313 can be introduced to the adsorption/desorption units 320, 325, respectively, such that the first purified n-paraffins product flows downward through the medium. The displacing medium via lines 361, 362 can be introduced to the adsorption/desorption units 320, 325, respectively, such that the displacing medium flows upwardly therethrough.

[0060] The second purified n-paraffins product via lines 327, 328 can be introduced to the separator 340 via line 329 and the impurities via lines 322, 323 can be introduced to the separator 350 via line 324. The separator 340 can provide the second purified n-paraffins product via line 313 and a recycle displacing medium via line 344. The recycle displacing medium in line 344 can be introduced to the separator 350 or directly recycled to a fresh or make-up displacing medium in line 360. The separator 350 can provide an impurity effluent via line 352 and a recycle displacing medium via line 354, which can be introduced to the make-up displacing medium in line 360. The recycle and make-up displacing medium in line 360 can provide the displacing mediums introduced via lines 361, 362 to the adsorption/desorption units 320, 325. The separators 340, 350 can separate the displacing medium from the n-paraffins-rich hydrocarbons and the n-paraffins-lean hydrocarbons using any suitable method. For example, the separator 340 can condense the second purified n-paraffins product to provide a condensed second purified n-paraffins product via line 133 and a gaseous recycle displacing medium via line 344. Similarly, the separator 350 can condense the impurities introduced via line 324 to provide a condensed impurity effluent via line 352 and the recycle displacing medium via line 354.

[0061] The displacing medium introduced to the first and second adsorption/desorption units 320, 325 can include any material capable of displacing the adsorbed impurities. Suitable displacing mediums can include materials in the same class of molecules as the predominant impurity to be removed from the first purified n-paraffins in line 309. For example, the predominant impurity to be removed from the first purified n-paraffins in line 309 can be aromatic hydrocarbons. As such, desorbents suitable for desorbing aromatic hydrocarbons can include nonpolar, alkyl-substituted benzene. For example, a suitable desorbent for desorbing aromatic hydrocarbons can be or include toluene.

[0062] The first purified n-paraffins product introduced via lines 311, 313 to the adsorption/desorption units 320, 326 can be contacted in the liquid and/or vapor phase with a solid adsorbent. In at least one specific embodiment, the adsorption of the impurities within the adsorption/desorption units 320, 325 can be performed in the liquid phase. The first purified n-paraffins product can be heated to a temperature of from about 200°C to about 250°C. Back pressure regulation can be used to promote or maintain the adsorption of the impurities in the liquid phase.

[0063] The adsorption/desorption beds 321, 326 can include any suitable medium capable of adsorbing one or more of any impurities that may be present in the first purified n-paraffins introduced to the adsorption/desorption units 320, 325, respectively. For example, the adsorption/desorption beds 321, 326 can include molecular sieves. Illustrative molecular sieves can include, but are not limited to, zeolites of the faujasite family, which includes natural and synthetic zeolites having an average pore diameter of from about 6 to about 15 Å. Representative examples of molecular sieves include faujasites, mordenites, and zeolite types X, Y, and A. The adsorbent can include an inorganic binder such as silica, alumina, silica-alumina, kaolin, and/or attapulgite. The zeolites can be subjected to cation exchange prior to use. Cations that can be incorporated into the zeolites, through ion-exchange processes, for example, include alkali and alkaline earth metals, as well as trivalent cations. The molecular sieves can be in any form, such as extruded, beaded, or crushed particles.

[0064] The adsorption and desorption of the impurities within the adsorption/desorption units 320, 325 can be carried out under liquid and/or vapor phase. The adsorption and desorption of the n-paraffins in the adsorption/desorption units 320, 325 can be carried out at a temperature ranging atmospheric temperature to about 250°C. For example, the adsorption of the impurities can be carried out in the liquid phase at a temperature of from about 100°C to about 150°C. Further adsorption and desorption process conditions and can be as discussed and described in U.S. Pat. Nos. 5,109,139; 5,171,923; and 5,220,099.

[0065] Embodiments of the present invention further relate to any one or more of the following paragraphs:

[0066] 1. A method for producing n-paraffins, comprising hydropyrolysis at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydropyrolysis kerosene product comprising n-paraffins; and separating the n-paraffins from the hydropyrolysis kerosene product to produce an n-paraffins product.

[0067] 2. The method according to paragraph 1, wherein the kerosene fraction is hydropyrolysed in the presence of hydrogen and one or more catalysts at a temperature of from about 200°C to about 420°C and a pressure of from about 3,000 kPa to about 8,000 kPa.

[0068] 3. The method according to paragraphs 1 or 2, wherein the hydropyrolysed kerosene fraction further comprises at least 1 ppmw nitrogen-containing compounds.

[0069] 4. The method according to any of paragraphs 1 to 3, wherein the hydropyrolysed kerosene fraction has a bromine index of at least 10.

[0070] 5. The method according to any of paragraphs 1 to 4, wherein the hydropyrolysed kerosene fraction further comprises at least 1 ppmw sulfur-containing compounds.

[0071] 6. The method according to any of paragraphs 1 to 5, wherein a kerosene fraction recovered from an atmospheric distillation unit is mixed with at least one of the thermally cracked hydrocarbon product and the hydropyrolysed kerosene product.

[0072] 7. The method according to any of paragraphs 1 to 6, wherein separating the n-paraffins comprises an adsorption process, a solvent extraction process, a distillation process, or any combination thereof.

[0073] 8. The method according to any of paragraphs 1 to 7, wherein separating the n-paraffins comprises an adsorption process comprising contacting the hydropyrolysed kerosene product with a first adsorbent material at conditions sufficient to cause the first adsorbent material to adsorb at least a portion of the n-paraffins; contacting the adsorbed n-paraffins with a displacing medium at temperatures sufficient to cause at least a portion of the adsorbed n-paraffins to be desorbed; and recovering the adsorbed n-paraffins as the n-paraffins product.

[0074] 9. The method according to paragraph 8, wherein the recovered n-paraffins comprise one or more impurities, and wherein the adsorption process further comprises con-
tacting the recovered n-paraffins with a second adsorbent material at conditions sufficient to cause the second adsorbent material to adsorb at least a portion of the one or more impurities to produce an n-paraffins product having a reduced concentration of impurities relative to the recovered n-paraffins.

[0075] 10. The method according to paragraph 9, wherein the impurities comprise aromatic hydrocarbons, and wherein the n-paraffins product has a concentration of less than about 100 ppmw aromatics.

[0076] 11. The method according to any of paragraphs 1 to 10, further comprising introducing an atmospheric distillation tower bottoms, a vacuum distillation tower bottoms, or a combination thereof to a thermal cracker to produce the thermally cracked hydrocarbon product; and separating the thermally cracked hydrocarbon product to produce a light hydrocarbon fraction, a heavy hydrocarbon fraction, and the kerosene fraction.

[0077] 12. A method for producing n-paraffins, comprising thermally cracking a hydrocarbon feed to produce a thermally cracked hydrocarbon mixture; selectively separating a kerosene fraction from the hydrocarbon mixture; hydrotreating at least a portion of the kerosene fraction to produce a hydrotreated kerosene comprising n-paraffins, less than about 500 ppmw sulfur-containing compounds, and less than about 200 ppmw nitrogen-containing compounds; and separating the n-paraffins from the hydrotreated kerosene product to produce an n-paraffins product.

[0078] 13. The method according to paragraph 12, wherein the hydrotreated kerosene comprises at least 1 ppmw nitrogen-containing compounds and at least 1 ppmw sulfur-containing compounds.

[0079] 14. The method according to paragraphs 12 or 13, wherein the kerosene fraction has a bromine index of at least 10.

[0080] 15. The method according to any of paragraphs 12 to 14, wherein the hydrocarbon feed comprises atmospheric distillation tower bottoms, vacuum distillation tower bottoms, or a combination thereof.

[0081] 16. The method according to any of paragraphs 12 to 15, wherein separating the n-paraffins comprises an adsorption process, a solvent extraction process, a distillation process, or any combination thereof.

[0082] 17. A system for producing n-paraffins, comprising a hydrotreating unit for hydrotreating at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydrotreated kerosene product comprising n-paraffins; and a first separation unit for separating the n-paraffins from the hydrotreated kerosene product to produce an n-paraffins product.

[0083] 18. The system according to paragraph 17, further comprising a thermal cracking unit for thermally cracking a hydrocarbon feed to produce the thermally cracked hydrocarbon product; and a second separation unit for separating the thermally cracked hydrocarbon product to produce a light hydrocarbon fraction, a heavy hydrocarbon fraction, and the kerosene fraction.

[0084] 19. The system according to paragraphs 17 or 18, wherein the first separation unit comprises one or more adsorption/desorption units.

[0085] 20. The system according to any of paragraphs 17 to 19, further comprising a third separation unit for purifying the n-paraffins product to produce an n-paraffins product comprising about 99 wt % or more n-paraffins.

[0086] Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits and ranges appear in one or more claims below. All numerical values are “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0087] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[0088] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A method for producing n-paraffins, comprising:
   - hydrotreating at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydrotreated kerosene product comprising n-paraffins; and
   - separating the n-paraffins from the hydrotreated kerosene product to produce an n-paraffins product.

2. The method of claim 1, wherein the kerosene fraction is hydrotreated in the presence of hydrogen and one or more catalysts at a temperature of from about 200°C to about 420°C and a pressure of from about 3.000 kPa to about 8.000 kPa.

3. The method of claim 1, wherein the hydrotreated kerosene fraction further comprises at least 1 ppmw nitrogen-containing compounds.

4. The method of claim 1, wherein the hydrotreated kerosene fraction has a bromine index of at least 10.

5. The method of claim 1, wherein the hydrotreated kerosene fraction further comprises at least 1 ppmw sulfur-containing compounds.

6. The method of claim 1, wherein a kerosene fraction recovered from an atmospheric distillation unit is mixed with at least one of the thermally cracked hydrocarbon product and the hydrotreated kerosene product.

7. The method of claim 1, wherein separating the n-paraffins comprises an adsorption process, a solvent extraction process, a distillation process, or any combination thereof.

8. The method of claim 1, wherein separating the n-paraffins comprises an adsorption process comprising:
   - contacting the hydrotreated kerosene product with a first adsorbent material at conditions sufficient to cause the first adsorbent material to adsorb at least a portion of the n-paraffins;
   - contacting the adsorbed n-paraffins with a displacing medium at conditions sufficient to cause at least a portion of the adsorbed n-paraffins to be desorbed; and
   - recovering the desorbed n-paraffins as the n-paraffins product.
n-paraffins with a second adsorbent material at conditions sufficient to cause the second adsorbent material to adsorb at least a portion of the one or more impurities to produce an n-paraffins product having a reduced concentration of impurities relative to the recovered n-paraffins.

10. The method of claim 9, wherein the impurities comprise aromatic hydrocarbons, and wherein the n-paraffins product has a concentration of less than about 100 ppmw aromatics.

11. The method of claim 1, further comprising:
introducing an atmospheric distillation tower bottoms, a vacuum distillation tower bottoms, or a combination thereof to a thermal cracker to produce the thermally cracked hydrocarbon product; and
separating the thermally cracked hydrocarbon product to produce a light hydrocarbon fraction, a heavy hydrocarbon fraction, and the kerosene fraction.

12. A method for producing n-paraffins, comprising:
thermally cracking a hydrocarbon feed to produce a thermally cracked hydrocarbon mixture;
selectively separating a kerosene fraction from the hydrocarbon mixture;
hydrocracking at least a portion of the kerosene fraction to produce a hydrotreated kerosene comprising n-paraffins, less than about 500 ppmw sulfur-containing compounds, and less than about 200 ppmw nitrogen-containing compounds; and
separating the n-paraffins from the hydrotreated kerosene product to produce an n-paraffins product.

13. The method of claim 12, wherein the hydrotreated kerosene comprises at least 1 ppmw nitrogen-containing compounds and at least 1 ppmw sulfur-containing compounds.

14. The method of claim 12, wherein the kerosene fraction has a bromine index of at least 10.

15. The method of claim 12, wherein the hydrocarbon feed comprises atmospheric distillation tower bottoms, vacuum distillation tower bottoms, or a combination thereof.

16. The method of claim 12, wherein separating the n-paraffins comprises an adsorption process, a solvent extraction process, a distillation process, or any combination thereof.

17. A system for producing n-paraffins, comprising:
a hydrocracking unit for hydrocracking at least a portion of a kerosene fraction recovered from a thermally cracked hydrocarbon product to produce a hydrotreated kerosene comprising n-paraffins; and
a first separation unit for separating the n-paraffins from the hydrotreated kerosene product to produce an n-paraffins product.

18. The system of claim 17, further comprising a thermal cracking unit for thermally cracking a hydrocarbon feed to produce the thermally cracked hydrocarbon product; and a second separation unit for separating the thermally cracked hydrocarbon product to produce a light hydrocarbon fraction, a heavy hydrocarbon fraction, and the kerosene fraction.

19. The system of claim 17, wherein the first separation unit comprises one or more adsorption/desorption units.

20. The system of claim 17, further comprising a third separation unit for purifying the n-paraffins product to produce an n-paraffins product comprising about 99 wt % or more n-paraffins.

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