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(54) Title: METHODS FOR PRODUCING LINEAR ALKYL BENZENES, PARAFFINS, AND OLEFINS FROM NATURAL OILS AND KEROSENE

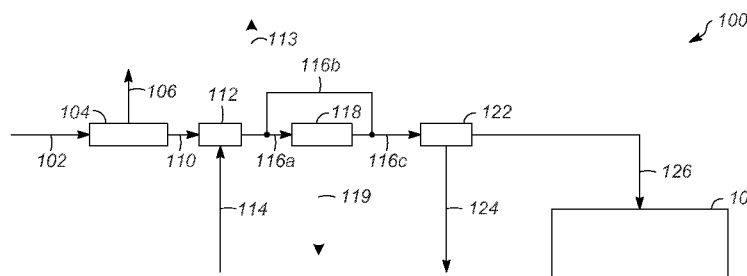


FIG. 1

(57) Abstract: A method for producing a linear paraffin product from natural oil and kerosene includes providing a first feed stream comprising kerosene, pre-fractionating the first feed stream to generate a paraffin stream comprising at least paraffins in a desired range, and combining paraffin stream with a second feed stream comprising natural oil to form a combined stream. The method further includes deoxygenating the natural oil and fractionating the combined stream to remove paraffins that are heavier than the desired range.

METHODS FOR PRODUCING LINEAR ALKYL BENZENES, PARAFFINS, AND
OLEFINS FROM NATURAL OILS AND KEROSENE

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 14/301,824 which was
5 filed June 11, 2014, the contents of which are hereby incorporated by reference in its
entirety.

FIELD OF THE INVENTION

[0002] The present invention relates generally to methods for producing renewable
detergent compounds, and more particularly relates to methods for producing linear
10 alkylbenzenes, paraffins, and olefins from natural oils and kerosene.

BACKGROUND OF THE INVENTION

[0003] While detergents made utilizing linear alkylbenzene-, paraffin-, and olefin-based
surfactants are biodegradable, processes for creating linear alkylbenzenes, paraffins, and
olefins are not based on renewable sources. Specifically, linear alkylbenzenes, paraffins,
15 and olefins are traditionally produced from kerosene extracted from the earth. Due to the
growing environmental concerns over fossil fuel extraction and economic concerns over
exhausting fossil fuel deposits, there is a demand for incorporating alternate feed sources
with the traditional kerosene feed source for producing biodegradable surfactants for use
in detergents and in other industries.

20 [0004] Accordingly, it is desirable to provide methods for producing linear
alkylbenzenes, paraffins, and olefins from a feed source that includes natural oils, i.e., oils
that are not extracted from the earth, in addition to kerosene. Furthermore, other desirable
features and characteristics of the present invention will become apparent from the
subsequent detailed description of the invention and the appended claims, when taken in
25 conjunction with the accompanying drawing and this background of the invention.

SUMMARY OF THE INVENTION

[0005] Methods for producing a linear alkylbenzene, paraffin, or olefin product from a
natural oil and kerosene feed source are provided herein. In accordance with an exemplary
embodiment, a method for producing a linear paraffin product from natural oil and

kerosene includes providing a first feed stream comprising kerosene, pre-fractionating the first feed stream to provide only two hydrocarbon stream, a lighter material stream and a remainder paraffin feed stream, and combining the remainder paraffin feed stream with a natural oil feed stream comprising natural oil to form a combined stream. The method further includes deoxygenating the natural oil and fractionating the combined stream to remove paraffins that are lighter than C10.

[0006] In another exemplary embodiment, a method for producing a linear olefin product from natural oil and kerosene includes providing a first feed stream comprising kerosene, pre-fractionating the first feed stream to produce a remainder paraffin feed stream comprising paraffins, and combining the remainder paraffin feed stream with a second feed stream comprising natural oil to form a combined stream. The method further includes deoxygenating the natural oil, fractionating the combined stream and removing paraffins that are heavier than desired to form a second paraffin stream, and dehydrogenating the second paraffin stream to form a stream comprising olefins.

[0007] In accordance with yet another exemplary embodiment, a method for producing a linear alkylbenzene product from natural oil and kerosene includes providing a first feed stream comprising kerosene, pre-fractionating the first feed stream to produce a remainder paraffin stream comprising paraffins, and combining the remainder paraffin stream with a second feed stream comprising natural oil to form a combined stream. The method further includes deoxygenating the natural oil, fractionating the combined stream and removing paraffins that are heavier than desired to form a second paraffin stream, dehydrogenating the second paraffin stream to form a stream comprising olefins, and alkylating the stream comprising olefins with a third feed stream comprising benzene to form a stream comprising alkylbenzenes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Embodiments of the present invention will hereinafter be described in conjunction with the following drawing figures, wherein:

[0009] FIG. 1 schematically illustrates an exemplary embodiment of a system utilizing a process for producing linear alkylbenzenes, paraffins, and/or olefins from natural oils and kerosene;

[0010] FIG. 2 illustrates an exemplary subsystem of the system shown in FIG. 1 for producing linear alkylbenzenes, paraffins, and/or olefins;

[0011] FIG. 3 schematically illustrates another exemplary embodiments of a system utilizing a process for producing linear alkylbenzenes, paraffins, and/or olefins from natural oils and kerosene;

[0012] FIG. 4 schematically illustrates another exemplary embodiment of a system utilizing a process for producing linear alkylbenzenes, paraffins, and/or olefins from natural oils and kerosene; and

[0013] FIG. 5 schematically illustrates yet another exemplary embodiment of a system utilizing a process for producing linear alkylbenzenes, paraffins, and/or olefins from natural oils and kerosene.

DETAILED DESCRIPTION

[0014] The following detailed description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0015] Various embodiments contemplated herein relate to methods for producing a linear alkylbenzene, paraffin, or olefin product from natural oils and kerosene. It will be appreciated that embodiments of the present disclosure allow for increased use of the C₁₀ content in the kerosene feed. As will be appreciated by those having ordinary skill in the art, only a certain percentage of C₁₀ (generally 10% to 15%) is allowed to be included in a linear alkylbenzene product for use in detergents. Traditionally, where only kerosene was used as a feed stock, any C₁₀ present in an amount beyond this maximum needed to be removed from the system and discarded or put to use for the production of other products. By supplementing the feed with a natural oil source, which generally has a higher content of heavier hydrocarbons, the producer can increase the use of C₁₀ from the kerosene feed while still maintaining the same 10%-15% content. Table 1, presented below, shows an exemplary illustration of the benefits realized by supplementing a kerosene feed with natural oils. Table 1 is provided merely for illustration, and is not limiting on the possible

benefits, carbon number-compositions, or natural oil/kerosene feed amounts realizable in accordance with the teachings of the present disclosure.

	<u>Example 1</u>	<u>Example 2</u>	<u>Feed 1/Feed 2</u>
Natural C12	34000	0	
Feed MTA	242726	527933	0.46
Extract MTA	74000	74087	
Product Purity	0.985	0.985	
Product Aromatics,	0.005	0.005	
Product C# Distribution			
nC9	0	0	
nC10	15.03	14.98	
nC11	15.11	32.82	
nC12	57.88	27.93	
nC13	10.29	22.35	
nC14	0.19	0.42	
	98.5	98.5	
AMW Target range	164.4	163.4	

5

Table 1

[0016] As shown in Table 1, in Example 1, 34,000 kg of natural oil are provided with 242,726 MTA feed (kerosene). The C₁₀ percentage in the product is 15%. In Example 2, however, a greater amount of feed MTA, 527,933 kg is required to achieve the same 15% C₁₀ product where no natural oils were provided. As such, in Example 1, a reduction of 54% MTA feed is realized ($\text{MTA Feed 1} / \text{Feed 2} = 0.46$, as shown in Table 1) by providing natural oils.

[0017] The process is also advantageous by capitalizing on several synergies between the kerosene feed and the natural oil feed. For example, it is likely that heavy hydrocarbons arising from both the kerosene feed and the natural oil feed will need to be separated, and so the location of a single separator is selected to address both needs. The heavies from the kerosene feed are not separated prior to combining the kerosene feed

with the natural oil feed, thereby eliminating one separation step. Similarly, a hydrotreating unit is positioned in the process to process material originating from both the kerosene feed and also material originating from the natural oil.

[0018] In FIG. 1, an exemplary system 100 utilizing an exemplary process for producing a linear alkylbenzene, paraffin, and/or olefin product is depicted. A kerosene (also known as paraffin oil) feed 102 is fed into a pre-fractionator 104. The pre-fractionator 104 fractionates the kerosene feed 102 into only two hydrocarbon streams 106 and 110. Stream 106 is a light hydrocarbon stream that includes, in one embodiment, C₉ hydrocarbons and lighter hydrocarbons (i.e., hydrocarbons having fewer carbons) that were separated from the kerosene feed 102. In other embodiments, stream 106 may include C₈ and lighter hydrocarbons or C₁₀ and lighter hydrocarbons, depending on the desired product composition of linear alkylbenzenes, paraffins, and olefins. Light hydrocarbon stream 106 is removed from the system 100 and may be used in other processes

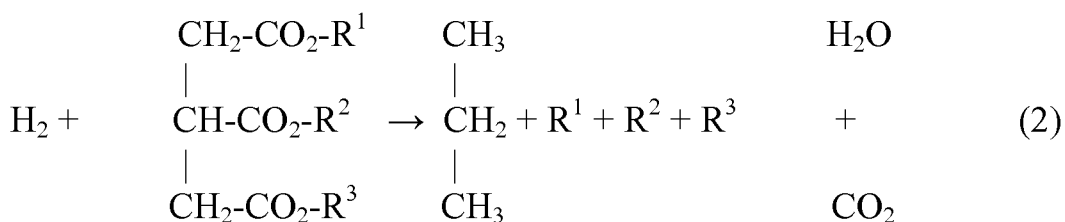
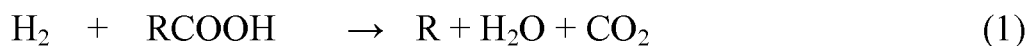
[0019] Remainder paraffin feed stream 110 includes hydrocarbons that are selected for further processing into the desired linear alkylbenzenes, paraffins, and olefins and also includes heavy distillate. For example, stream 110, in one embodiment, includes at least C₁₀ – C₁₃ hydrocarbons or C₁₀ – C₁₉ hydrocarbons. Stream 110 may include any range of hydrocarbons within the C₉ – C₁₉ range. Heavier hydrocarbons are not separated at this point in the process in order to take advantage of a later separator used to separate heavier hydrocarbons originating from feed 102 and also originating from natural oil feed 114 feed discussed below. Therefore, stream 110 also may include hydrocarbons heavier than those targeted for processing into the linear alkylbenzenes, paraffins and olefins including C₂₀ and greater carbon number hydrocarbons. Pre-fractionator 104 produces only the two hydrocarbon streams, stream 106 with C₉ and lighter hydrocarbons and stream 110 with C₁₀ and heavier hydrocarbons. Pre-fractionator 104 does not product a third heavy distillate hydrocarbon stream containing hydrocarbons heavier than those of stream 110. Capital costs and operating costs are reduced by using another separation unit downstream to separate any hydrocarbons greater than desired for further processing into the desired linear alkyl benzenes paraffins and olefins.

[0020] With continued reference to FIG. 1, in an exemplary embodiment, stream 110 continues within system 100 for further processing in a kero-hydrotreater (KHT) 112.

KHT 112 is employed to treat hydrocarbons in stream 110 to reduce the naturally occurring nitrogen and sulfur content in kerosene to acceptable levels for use in detergents. KHT 112 is a catalyst-based apparatus, and various catalysts for denitrification and desulfurization are known to those having ordinary skill in the art. In the embodiment depicted in FIG. 1, the KHT 112 also receives a feed stream of natural oil 114. Stream 110 and natural oil stream 114 may be combined prior to KHT 112 or each stream may be introduced to KHT 112 separately. As used herein, natural oils are those derived from plant or algae matter, and are often referred to as renewable oils. Natural oils are not based on kerosene or other fossil fuels. In certain embodiments, the natural oils include, but are not limited to, one or more of coconut oil, babassu oil, castor oil, algae 1 byproduct, beef tallow oil, borage oil, camelina oil, Canola ® oil, choice white grease, coffee oil, corn oil, *Cuphea Viscosissima* oil, evening primrose oil, fish oil, hemp oil, hepar oil, jatropha oil, *Lesquerella Fendleri* oil, linseed oil, *Moringa Oleifera* oil, mustard oil, neem oil, palm oil, palm kernel oil, perilla seed oil, poultry fat, rice bran oil, soybean oil, stillingia oil, sunflower oil, tung oil, yellow grease, cooking oil, and other vegetable, nut, or seed oils. Other natural oils will be known to those having ordinary skill in the art. The natural oils typically include triglycerides, free fatty acids, or a combination of both, and other trace compounds.

[0021] In embodiments where, as in FIG. 1, the natural oil feed 114 and stream 110 are combined in the KHT 112, the KHT is also configured to deoxygenate the natural oil feed 114 to produce paraffins. The triglycerides and fatty acids in the natural oil feed 114 are deoxygenated and converted into linear paraffins in the KHT 112, using a catalyst that is suitable for both deoxygenation and denitrification/desulfurization or a mix of catalysts that each accomplish one or more of deoxygenation, denitrification, and desulfurization. A suitable KHT 112 apparatus for use in embodiments of the present disclosure is sold by UOP LLC. Structurally, triglycerides are formed by three, typically different, fatty acid molecules that are bonded together with a glycerol bridge. The glycerol molecule includes three hydroxyl groups (HO-), and each fatty acid molecule has a carboxyl group (COOH). In triglycerides, the hydroxyl groups of the glycerol join the carboxyl groups of the fatty acids to form ester bonds. Therefore, during deoxygenation, the fatty acids are freed from the triglyceride structure and are converted into linear paraffins. The glycerol is converted into propane, and the oxygen in the hydroxyl and carboxyl groups is converted into either

water or carbon dioxide. The propane, water and carbon dioxide may be removed in stream 113. The deoxygenation reaction for fatty acids (1) and triglycerides (2) are illustrated, respectively, as:



During the deoxygenation reaction, the length of a product paraffin chain R^n will vary by a value of one depending on the exact reaction pathway. For example, if carbon dioxide is formed, then the chain will have one fewer carbon than the fatty acid source (R^n). If water is formed, then the chain will match the length of the R^n chain in the fatty acid source. Typically, due to the reaction kinetics, water and carbon dioxide are formed in roughly equal amounts, such that equal amounts of C_x paraffins and C_{x-1} paraffins are formed.

[0022] In some embodiments, a treated stream of paraffins 116a exiting KHT 112 may be fed to a separator 118 to separate the desirable linear paraffins from branched or cyclic compounds that may be included in the stream 116a. Non-normal paraffins may be removed in stream 119. A suitable separator for this purpose is a separator that operates using the UOP LLC Molex® process, which is a liquid-state separation of normal paraffins from branched and cyclic components using UOP LLC Sorbex® technology. Other separators known in the art are suitable for use herein as well. In other embodiments, depending on the composition of the kerosene feed 102 and/or the natural oil feed 114, separation of normal paraffins from branched and cyclic components is not necessary, and a treated stream of paraffins 116b from the KHT 112 may be directed downstream for further processing.

[0023] A linear paraffin stream 116c exiting the separator 118, or the treated stream of paraffins 116b, is fed to a fractionator 122. As discussed above, the pre-fractionator 104 removed light hydrocarbons from the kerosene feed 102; however, kerosene feed and the natural oil feed 114 includes hydrocarbons that are heavier than the desired range, and as

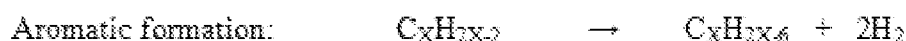
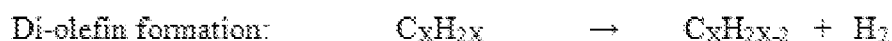
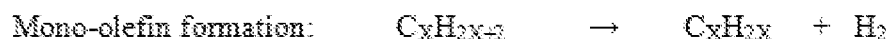
such the fractionator 122 is provided to fractionate hydrocarbons that are heavier than the desired range. In one embodiment, hydrocarbons that are C_{14} and heavier are removed from system 100 in a heavy paraffins stream 124, and may be used in other processes. In other embodiments, hydrocarbons anywhere in the range from $C_{15} - C_{18}$ and heavier are removed from system 100 in the heavy paraffins stream 124. Separating the heavier hydrocarbons at this point in the process reduces the overall cost of the process. The paraffins in the desired range exit the fractionator 122 in a stream 126 for further processing into linear alkylbenzene, paraffin, and/or olefin products in subsystem 10, as will be described in greater detail below.

[0024] In FIG. 2, an exemplary subsystem 10 utilizing an exemplary process for producing a linear alkylbenzene, paraffin, or olefin product is depicted. Subsystem 10 receives as its feed stream the stream 126 from the fractionator 122 including the desired of linear paraffins. Optionally, Stream 126 may be fed to a separator (not shown) such as a multi-stage fractionation unit, distillation system, or similar known apparatus, to separate the paraffins into various desirable fractions, or into various portions for producing one or more of linear alkylbenzenes, paraffins, and olefins if desired. Any number of paraffin portions may be generated and one or more portions may include the same hydrocarbon range as another portion, or they may be separated into different fractions. The separation is performed after hydrotreating in order to take advantage of synergies provided by the separator all ready present after the hydrotreating unit. For example, where the desired range is selected as $C_{10} - C_{18}$, one portion may include $C_{10} - C_{13}$ paraffins, whereas another portion may include $C_{14} - C_{18}$ paraffins. Alternatively, they may both include $C_{10} - C_{18}$ paraffins. In another example, where the desired range is selected as $C_{10} - C_{13}$, two portions or more portions may include hydrocarbons in that range. Numerous other examples are possible, depending on the quantity and the hydrocarbon content of the desired product linear alkylbenzenes, paraffins, and/or olefins.

[0025] The paraffins may thereafter be purified to remove trace contaminants, resulting in a purified paraffin product. In some embodiments, wherein only paraffin production is desired, the entire paraffin product (i.e., all of the one or more portions) may be purified at this stage. In other embodiments, some of the paraffin product is directed to further processing stages for the production of alkylbenzenes and/or olefins. In still other embodiments, wherein only olefin and/or alkylbenzene production is desired, the entire

paraffin product (i.e., all of the one or more portions) may be directed to further processing stages. Any paraffin portion may be directed to a purification system to remove any remaining trace contaminants, such as oxygenates, nitrogen compounds, and sulfur compounds, among others, that were not previously removed in the processing steps described above. In one example, purification system is an adsorption system. Alternatively or additionally, a PEP unit, available from UOP LLC, may be employed as part of purification system. Subsequent to purification, a purified paraffins stream is removed from the system as the paraffin product.

[0026] As further shown in FIG. 2, paraffins 126 is introduced to a linear alkylbenzene and olefin production zone 28. Specifically, paraffins 126 is fed into a dehydrogenation unit 30 in the linear alkylbenzene and olefin production zone 28. In the dehydrogenation unit 30, the paraffins 126 is dehydrogenated into mono-olefins of the same carbon numbers as paraffins 126. Typically, dehydrogenation occurs through known catalytic processes, such as the commercially popular Pacol process. Conversion is typically less than 30%, for example less than 20%, leaving greater than 70% paraffins unconverted to olefins. Di-olefins (i.e., dienes) and aromatics are also produced as an undesired result of the dehydrogenation reactions as expressed in the following equations:



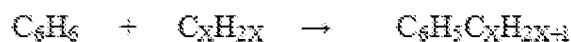
[0027] In FIG. 2, a dehydrogenated stream 32 exits the dehydrogenation unit 30 comprising mono-olefins and hydrogen, unconverted paraffins, as well as some byproduct di-olefins and aromatics. The dehydrogenated stream 32 is delivered to a phase separator 34 for removing the hydrogen from the dehydrogenated stream 32. The removed hydrogen can be directed away from system 100, or it can be used as fuel or as a source of hydrogen (H₂) for a deoxygenation process.

[0028] At the phase separator 34, a liquid stream 38 is formed and includes the mono-olefins, the unconverted paraffins, and any di-olefins and aromatics formed during

dehydrogenation. The liquid stream 38 exits the phase separator 34 and enters a selective hydrogenation unit 40. In one exemplary embodiment, the hydrogenation unit 40 is a DeFine® reactor (or a reactor employing a DeFine® process), available from UOP LLC. The hydrogenation unit 40 selectively hydrogenates at least a portion of the di-olefins in the liquid stream 38 to form additional mono-olefins. As a result, an enhanced stream 42 is formed with an increased mono-olefin concentration.

[0029] As shown, the enhanced stream 42 passes from the hydrogenation unit 40 to a light hydrocarbons separator 44, such as a stripper column, which removes a light end stream 46 containing any light hydrocarbons, such as butane, propane, ethane and methane, that resulted from cracking or other reactions during upstream processing. With the light hydrocarbons 46 removed, stream 48 is formed and may be delivered to an aromatic removal apparatus 50, such as a PEP unit available from UOP LLC. As indicated by its name, the aromatic removal apparatus 50 removes aromatics from the stream 48 and forms a stream of mono-olefins and unconverted paraffins 52.

[0030] In FIG. 2, to produce linear alkylbenzenes, the stream of mono-olefins 52 and a stream of benzene 54 are fed into an alkylation unit 56. The alkylation unit 56 holds a catalyst 58, such as a solid acid catalyst, that supports alkylation of the benzene 54 with the mono-olefins 52. Hydrogen fluoride (HF) and aluminum chloride (AlCl₃) are two major catalysts in commercial use for the alkylation of benzene with linear mono-olefins and may be used in the alkylation unit 56. Additional catalysts include zeolite-based or fluoridate silica alumina-based solid bed alkylation catalysts (for example, FAU, MOR, UZM-8, Y, X RE exchanged Y, RE exchanged X, amorphous silica-alumina, and mixtures thereof, and others known in the art). As a result of alkylation, alkylbenzene, typically called linear alkylbenzene (LAB), is formed according to the reaction:



and are present in an alkylation effluent 60.

[0031] To optimize the alkylation process, surplus amounts of benzene 54 are supplied to the alkylation unit 56. Therefore, the alkylation effluent 60 exiting the alkylation unit 56 contains alkylbenzene and unreacted benzene. Further, the alkylation effluent 60 may also

include some unreacted paraffins. In FIG. 2, the alkylation effluent 60 is passed to a benzene separation unit 62, such as a fractionation column, for separating the unreacted benzene from the alkylation effluent 60. This unreacted benzene exits the benzene separation unit 62 in a benzene recycle stream 64 that is delivered back into the alkylation unit 56 to reduce the volume of fresh benzene needed in stream 54.

[0032] As shown, a benzene-stripped stream 66 exits the benzene separation unit 62 and enters a paraffinic separation unit 68, such as a fractionation column. In the paraffinic separation unit 68, unreacted paraffins are removed from the benzene-stripped stream 66 in a recycle paraffin stream 70, and can be routed to and mixed with the first portion of paraffins 126 before dehydrogenation as described above, or can optionally be directed to the 122 for purification of product paraffins.

[0033] Further, an alkylbenzene stream 72 is separated by the paraffinic separation unit 68 and is fed to an alkylate separation unit 74. The alkylate separation unit 74, which may be, for example, a multi-column fractionation system, separates a heavy alkylate bottoms stream 76 from the alkylbenzene stream 72.

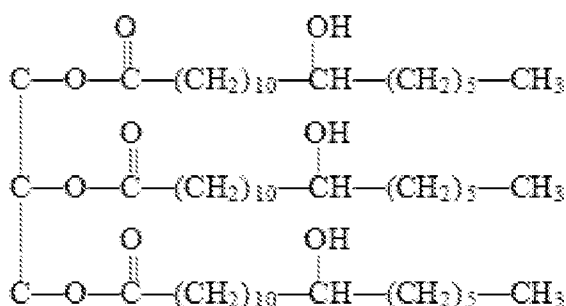
[0034] As a result of the post-alkylation separation processes, the linear alkylbenzene product 12 is isolated and exits the subsystem 10. It is noted that such separation processes are not necessary in all embodiments in order to isolate the alkylbenzene product 12. For instance, the alkylbenzene product 12 may be desired to have a wide range of carbon chain lengths and not require any fractionation to eliminate carbon chains longer than desired, i.e., heavies or carbon chains shorter than desired, i.e., lights. Further, the feed 114 may be of sufficient quality that no fractionation is necessary for the desired chain length range.

[0035] In FIG. 2, to produce linear olefins, a stream 53, which may include all or a portion of stream 52, is directed to a separator 57 for separating the unconverted paraffins from the olefins. In one particular embodiment, the separator 57 is an Olex[®] separator, available from UOP LLC. The Olex[®] process involves the selective adsorption of a desired component (i.e., olefins) from a liquid-phase mixture by continuous contacting with a fixed bed of adsorbent. In another particular embodiment, the separator 57 is a direct sulfonation separator. The separated, unconverted paraffins may optionally be directed back to the paraffin stream 24 for dehydrogenation for conversion to olefins (stream 71).

[0036] In FIG. 2, an olefins stream 61 exits the separator 57 and is fed to a separator 63. The separator 63 may be a multi-stage fractionation unit, distillation system, or similar known apparatus. The separator 63 may provide a means to separate the olefins into various desirable fractions. For example, as shown in FIG. 2, a first portion of olefins 65 and a second portion of olefins 65 are illustrated, although any number of olefin portions may be provided, depending on how many olefin fractions are desired. In certain embodiments, the first portion of olefins 65 has carbon chain lengths of C_{10} to C_{14} . In other embodiments, the first portion of olefins 65 has carbon chain lengths having a lower limit of C_L , where L is an integer from four (4) to thirty-one (31), and an upper limit of C_U , where U is an integer from five (5) to thirty-two (32). The second portion of olefins 67 may have carbon chains shorter than, longer than, or a combination of shorter and longer than, the chains of the first portion of olefins 65. In one particular embodiment, the first portion of olefins 65 includes olefins with C_{10} to C_{14} chains and the second portion of olefins 67 includes olefins with C_{18} to C_{20} chains. Subsequent to separation, the purified olefins portions 65 and 67 are removed from the subsystem 10 as the olefin product.

[0037] With reference now to exemplary natural oil feeds 114 of FIG. 1 that may be supplied to system 100, in addition to the kerosene feed 102, in certain embodiments, the feed 114 is substantially homogeneous and includes free fatty acids within a desired range. For instance, the feed may be palm fatty acid distillate (PFAD). Alternatively, the feed 114 may include triglycerides and free fatty acids that all have carbon chain lengths appropriate for a desired linear alkylbenzene product 12, linear paraffin product 13, or linear olefin products 65, 67.

[0038] In certain embodiments, the natural oil source is castor, and the feed 114 includes castor oils. Castor oils consist essentially of C_{18} fatty acids with additional, internal hydroxyl groups at the carbon-12 position. For instance, the structure of a castor oil triglyceride is:



During deoxygenation of a feed 114 comprising castor oil, it has been found that some portion of the carbon chains are cleaved at the carbon-12 position. Thus, deoxygenation creates a group of lighter paraffins having C₁₀ to C₁₁ chains resulting from cleavage during deoxygenation, and a group of non-cleaved heavier paraffins having C₁₇ to C₁₈ chains. With reference again to subsystem 10 in FIG. 2, the lighter paraffins may form the first portion of paraffins 24 and the heavier paraffins may form another portion of paraffins. However, the second portion of paraffins is not separated at this point in order to take advantage of a separator later in the process. It should be noted that while castor oil is shown as an example of an oil with an additional internal hydroxyl group, others may exist. Also, it may be desirable to engineer genetically modified organisms to produce such oils by design. As such, any oil with an internal hydroxyl group may be a desirable feed oil.

[0039] FIG. 3 depicts a system 200 using another exemplary embodiment of a process for producing a linear alkylbenzene, paraffin, or olefin from natural oil and kerosene. In this embodiment, the heavy paraffins stream 124 is not directed out of the system 200 for optional use in other processes as in FIG. 1, but rather is directed to a second subsystem 10b (stream 126 being directed to a first subsystem 10a) for the production of linear alkylbenzenes, paraffins, and/or olefins that are heavier than those used in the first subsystem. Subsystems 10a and 10b operate in the same manner as described above with regard to subsystem 10. In one example, subsystems 10a and 10b are separate systems for the simultaneous processing of the desired and the heavier paraffins, respectively. In other examples, subsystems 10a and 10b are the same system, wherein the desired range and heavier paraffins are processed at different times.

[0040] FIG. 4 depicts a system 300 using yet another exemplary embodiment of a process for producing a linear alkylbenzene, paraffin, or olefin from natural oil and

kerosene. In this embodiment, the natural oil feed stream 114 is deoxygenated into paraffins in a deoxygenation apparatus 113 prior to being combined with the paraffins from the kerosene feed 102. As such, the KHT 112 does not need to be configured for deoxygenation, and a catalyst used therein can be selected solely for denitrification and desulfurization purposes. In one example, a stream 115a of paraffins exits the deoxygenation apparatus 113 and is fed to the separator 118 where separation of branched and aromatic compounds is required. In an alternative example, a stream 115b of paraffins is combined with the kerosene paraffins downstream of the separator 118, where such separation is not required. In this embodiment, the heavy paraffins may either be removed from system 300 as discussed above with regard to FIG. 1 (stream 124a), or further processed into linear alkylbenzenes, paraffins, and/or olefins as discussed above with regard to FIG. 3.

[0041] FIG. 5 depicts a system 400 using still another exemplary embodiment of a process for producing a linear alkylbenzene, paraffin, or olefin from natural oil and kerosene. In this embodiment, heavy paraffins stream 124 is directed to an isomerization reactor 125. The isomerization reactor 125 is provided to convert the heavy linear paraffins stream 124 into a stream of branched paraffins and other compounds 127, which have other industrial uses such as fuel.

SPECIFIC EMBODIMENTS

[0042] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0043] A first embodiment of the invention is a method for producing a linear paraffin product from natural oil and kerosene comprising providing a first feed stream comprising kerosene; pre-fractionating the first feed stream to provide only two hydrocarbon streams, a light hydrocarbon stream comprising hydrocarbons having C9 or fewer carbon atoms and a remainder paraffin feed stream comprising the remaining paraffins having carbon numbers greater than C9; combining the remainder paraffin feed stream with a natural oil feed stream comprising natural oil to form a combined stream and deoxygenating the natural oil to form paraffins and generate a paraffin effluent stream; separating the paraffin effluent stream into a linear paraffin stream and a non-linear paraffin stream fractionating

the linear paraffin product to separate a linear paraffin stream comprising linear paraffins having 14 or more carbon atoms and a linear paraffin product stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein deoxygenating the natural oil comprises catalytically deoxygenating the natural oil prior to, at the same time as, or after combining the remainder paraffin feed stream with the natural oil feed stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising denitrifying and desulfurizing the remainder paraffin feed stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising separating one or more of branched hydrocarbons and cyclic hydrocarbons from the combined stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising dehydrogenating the paraffin product stream to generate a stream comprising olefins.

[0044] A second embodiment of the invention is a method for producing a linear olefin product from natural oil and kerosene comprising providing a first feed stream comprising kerosene; pre-fractionating the first feed stream to provide only two hydrocarbon streams, a light hydrocarbon stream comprising hydrocarbons having C9 or fewer carbon atoms and a remainder paraffin feed stream comprising the remaining paraffins having carbon numbers greater than C9; combining the remainder paraffin feed stream with a natural oil feed stream comprising natural oil to form a combined stream and deoxygenating the natural oil to form paraffins and generate a paraffin effluent stream; dehydrogenating the paraffin effluent stream to form a stream comprising olefins; separating the stream comprising olefins to separate a hydrocarbon stream comprising olefins having 14 or more carbon atoms and a linear olefin product stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising purifying the linear olefin product stream comprising olefins to form a purified stream comprising olefins. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising separating olefins from the purified stream comprising olefins, wherein separating olefins from the purified stream comprising olefins

comprises separating olefins using direct sulfonation or wherein separating olefins from the purified stream comprising olefins comprises separating olefins using selective adsorption from a liquid phase mixture by continuous contact with a fixed-bed adsorbent.

An embodiment of the invention is one, any or all of prior embodiments in this paragraph

5 up through the second embodiment in this paragraph, wherein a hydrogen stream produced

from dehydrogenating the paraffin effluent stream to form a stream comprising olefins is recycled for use in deoxygenating the natural oil and hydrotreating the kerosene feed. An

embodiment of the invention is one, any or all of prior embodiments in this paragraph up

through the second embodiment in this paragraph, further comprising passing the

10 hydrocarbon stream comprising linear paraffins having 14 or more carbon atoms to a

linear olefin, an alkylbenzene, or a linear olefin and alkylbenzene production subsystem for the production of heavy linear olefins and alkylbenzenes. An embodiment of the

invention is one, any or all of prior embodiments in this paragraph up through the second

embodiment in this paragraph, further comprising passing the linear paraffin stream

15 comprising linear paraffins having 14 or more carbon atoms to an isomerization reactor for

the production of branched olefins.

[0045] A third embodiment of the invention is a method for producing a linear

alkylbenzene product from natural oil and kerosene comprising providing a first feed stream comprising kerosene; pre-fractionating the first feed stream to provide only two

20 hydrocarbon streams, a light hydrocarbon stream comprising hydrocarbons having C9 or

fewer carbon atoms and a remainder paraffin feed stream comprising the remaining

paraffins having carbon numbers greater than C9; combining the remainder paraffin feed

stream with a second feed stream comprising natural oil and deoxygenating the natural oil

to form paraffins, and generate a combined stream; dehydrogenating the combined stream

25 to form a first olefin stream comprising olefins; fractionating the first olefin stream to

separate a second olefin stream comprising olefins having 14 or more carbon atoms and an

olefin product stream alkylating the olefin product stream with a third feed stream

comprising benzene to form a stream comprising alkylbenzenes. An embodiment of the

invention is one, any or all of prior embodiments in this paragraph up through the third

30 embodiment in this paragraph, wherein alkylating the stream comprising olefins with the

third feed stream comprising benzene comprises catalytically alkylating the stream

comprising olefins with the third feed stream comprising benzene using a hydrogen

fluoride or an aluminum chloride catalyst, or solid bed alkylation catalysts comprising fluoridated silica alumina or zeolites comprising one or more of FAU, MOR, UZM-8, Y, X RE exchanged Y, RE exchanged X, amorphous silica-alumina, and mixtures thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph, further comprising separating unreacted benzene from the stream comprising alkylbenzenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph, further comprising recycling unreacted benzene to the third feed stream comprising benzene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph, further comprising separating heavy alkylate bottoms from the stream comprising alkylbenzenes. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph, wherein combining the remainder paraffin feed stream with a second feed stream comprising natural oil comprises combining the remainder paraffin feed stream with a second feed stream comprising a natural oil chosen from the group comprising coconut oil, babassu oil, castor oil, algae 1 byproduct, beef tallow oil, borage oil, camelina oil, Canola oil, choice white grease, coffee oil, corn oil, Cuphea Viscosissima oil, evening primrose oil, fish oil, hemp oil, hepar oil, jatropha oil, Lesquerella Fendleri oil, linseed oil, Moringa Oleifera oil, mustard oil, neem oil, palm oil, palm kernel oil, perilla seed oil, poultry fat, rice bran oil, soybean oil, stillingia oil, sunflower oil, tung oil, yellow grease, cooking oil, and mixtures thereof.

[0046] While at least one exemplary embodiment has been presented in the foregoing detailed description, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

CLAIMS

1. A method for producing a linear paraffin product from natural oil and kerosene comprising:
 - providing a first feed stream comprising kerosene;
 - 5 pre-fractionating the first feed stream to provide only two hydrocarbon streams, a light hydrocarbon stream comprising hydrocarbons having C₉ or fewer carbon atoms and a remainder paraffin feed stream comprising the remaining paraffins having carbon numbers greater than C₉;
 - combining the remainder paraffin feed stream with a natural oil feed stream
 - 10 comprising natural oil to form a combined stream and deoxygenating the natural oil to form paraffins and generate a paraffin effluent stream; and
 - separating the paraffin effluent stream into a linear paraffin stream and a non-linear paraffin stream
 - fractionating the linear paraffin product to separate a linear paraffin stream
 - 15 comprising linear paraffins having 14 or more carbon atoms and a linear paraffin product stream;
 - or
 - dehydrogenating the paraffin effluent stream to form a stream comprising olefins;
 - separating the stream comprising olefins to separate a hydrocarbon stream comprising
 - 20 olefins having 14 or more carbon atoms and a linear olefin product stream.
2. The method of claim 1, wherein deoxygenating the natural oil comprises catalytically deoxygenating the natural oil prior to, at the same time as, or after combining the remainder paraffin feed stream with the natural oil feed stream.
3. The method of claim 1, further comprising denitrifying and desulfurizing the
- 25 remainder paraffin feed stream.
4. The method of claim 1, further comprising separating one or more of branched hydrocarbons and cyclic hydrocarbons from the combined stream.

5. The method of claim 1 further comprising dehydrogenating the paraffin product stream to generate a stream comprising olefins.

6. The method of claim 1, further comprising purifying the linear olefin product stream comprising olefins to form a purified stream comprising olefins.

5 7. The method of claim 6, further comprising separating olefins from the purified stream comprising olefins, wherein separating olefins from the purified stream comprising olefins comprises separating olefins using direct sulfonation or wherein separating olefins from the purified stream comprising olefins comprises separating olefins using selective adsorption from a liquid phase mixture by continuous contact with a fixed-bed adsorbent.

10 8. The method of claim 1, wherein a hydrogen stream produced from dehydrogenating the paraffin effluent stream to form a stream comprising olefins is recycled for use in deoxygenating the natural oil and hydrotreating the kerosene feed.

9. The method of claim 1, further comprising passing the hydrocarbon stream comprising linear paraffins having 14 or more carbon atoms to a linear olefin, an
15 alkylbenzene, or a linear olefin and alkylbenzene production subsystem for the production of heavy linear olefins and alkylbenzenes.

10. The method of claim 1, further comprising passing the linear paraffin stream comprising linear paraffins having 14 or more carbon atoms to an isomerization reactor for the production of branched olefins.

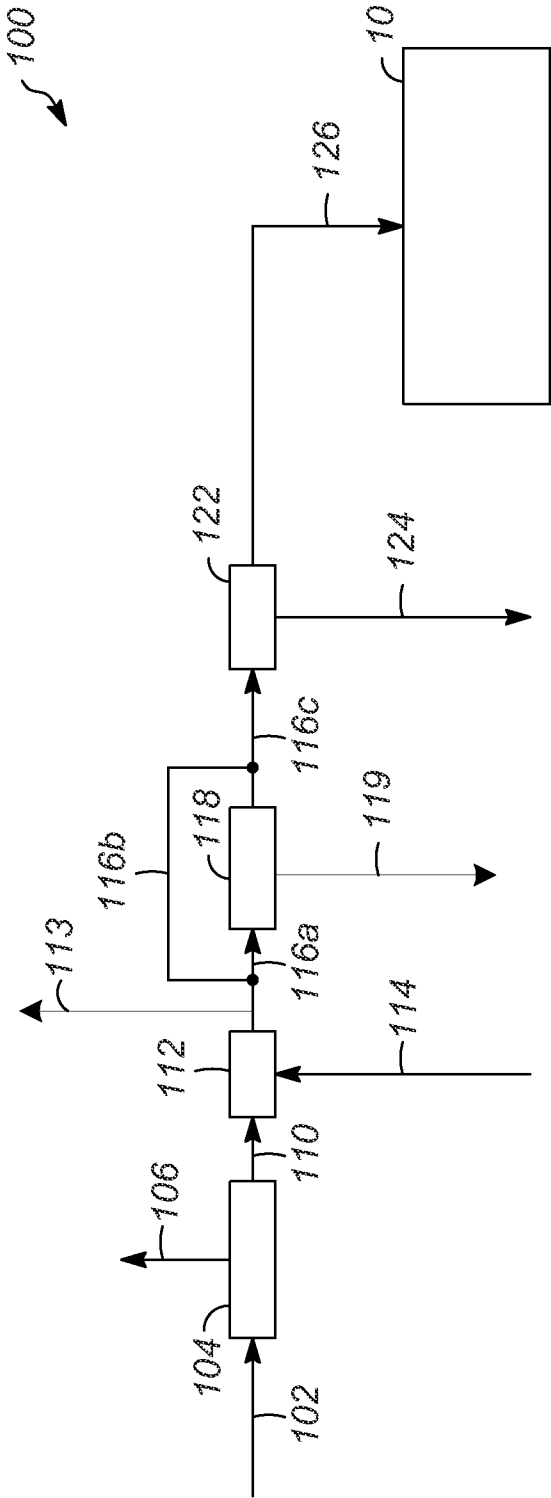


FIG. 1

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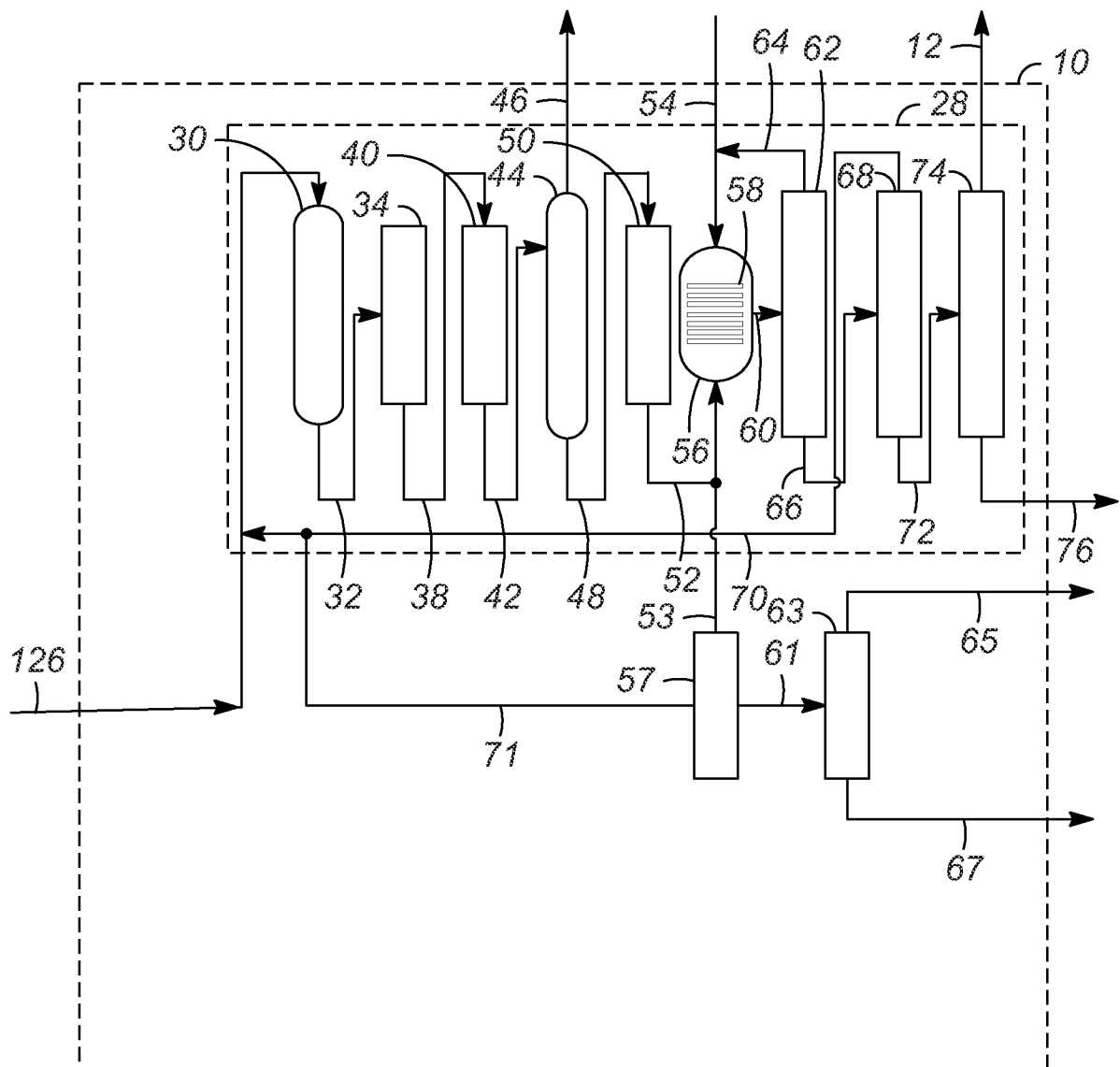


FIG. 2

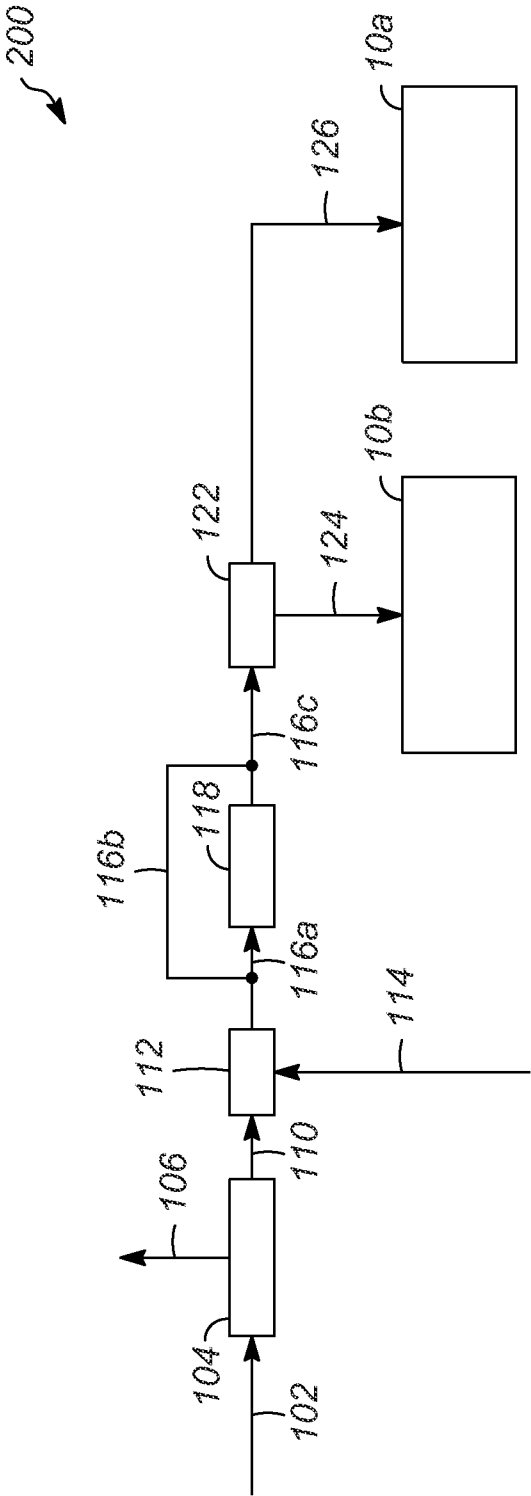


FIG. 3

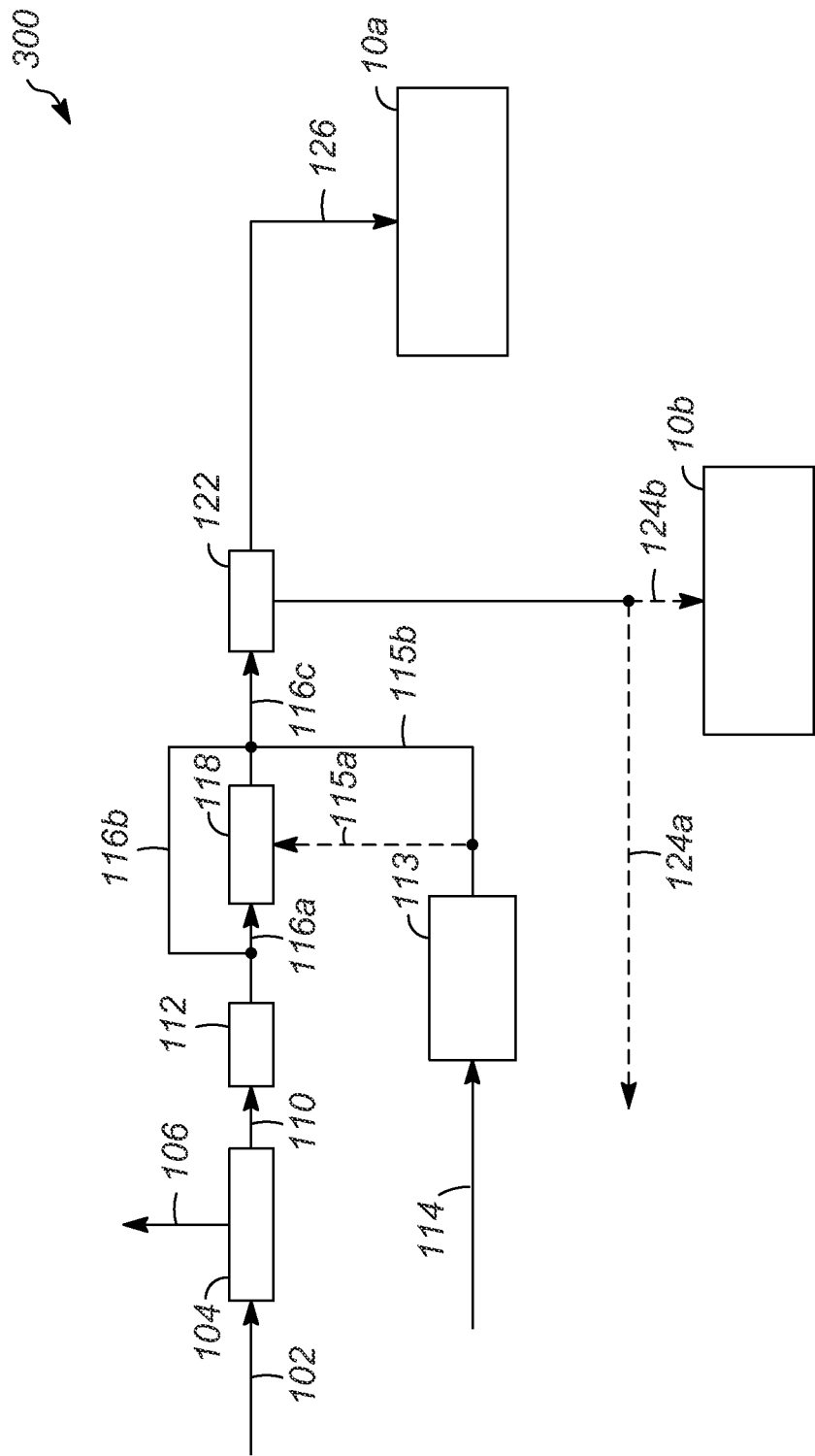


FIG. 4

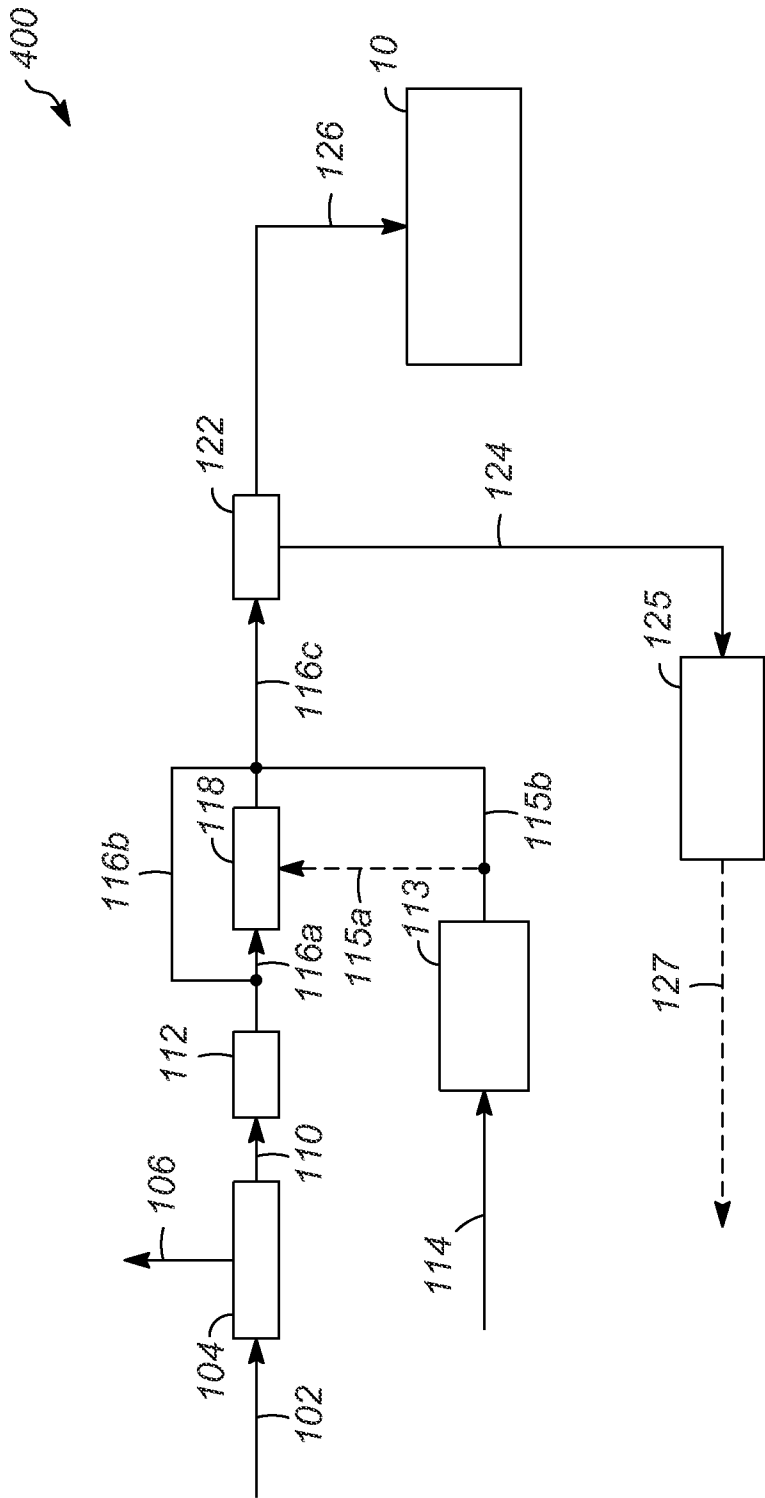


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/034334

A. CLASSIFICATION OF SUBJECT MATTER		
<i>C07C 5/327 (2006.01)</i> <i>C07C 5/333 (2006.01)</i> <i>C07C 7/04 (2006.01)</i> <i>C07C 1/20 (2006.01)</i> <i>C07C 7/12 (2006.01)</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C07C 5/327, 5/333, 7/04, 1/20, 7/12, 1/24, 1/22, 1/04, C10L 1/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
VINITI DB, EAPATIS, Espacenet, PAJ, USPTO, CIPO, DEPATISnet, Patentscope, PatSearch (RUPTO internal)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0253241 A1 (UOP LLC) 26.09.2013, claims, fig. 1-5, Table 1, paragraphs [0016] - [0023], [0030] - [0034], [0037] - [0039]	1-10
A	US 2013/0253240 A1 (UOP LLC) 26.09.2013	1-10
A	WO 2013/141978 A1 (UOP LLC) 26.09.2013	1-10
A	WO 2013/141979 A1 (UOP LLC) 26.09.2013	1-10
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier document but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family	
Date of the actual completion of the international search 14 August 2015 (14.08.2015)	Date of mailing of the international search report 17 September 2015 (17.09.2015)	
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer E. Guseva Telephone No. (495)531-64-81	