(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 December 2014 (18.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/200892 A1

(51) International Patent Classification:
C07C 7/00 (2006.01) *C07C 2/58* (2006.01)
C07C 7/20 (2006.01)

(21) International Application Number:
PCT/US2014/041494

(22) International Filing Date:
9 June 2014 (09.06.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/833,354 10 June 2013 (10.06.2013) US

(71) Applicant: **UOP LLC** [US/US]; 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventors: **FREY, Stanley J.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **ELLIG, Daniel L.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **BOZZANO, Andrea G.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **FICHTL, Geoffrey W.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **MAJUMDER, Debarshi**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: **MAAS, Maryann**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

[Continued on next page]

(54) Title: LINEAR ALKYLBENZENES FROM NATURAL OILS AND METHODS OF PRODUCING

(57) Abstract: The production of linear alkylbenzene from a natural oil is provided. A method comprises the step of deoxygenating the natural oils to form a stream comprising paraffins. The paraffins are dehydrogenated to provide mono-olefins. Then, benzene is alkylated with the mono-olefins under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene. Thereafter, the alkylbenzenes are isolated to provide the alkylbenzene product.

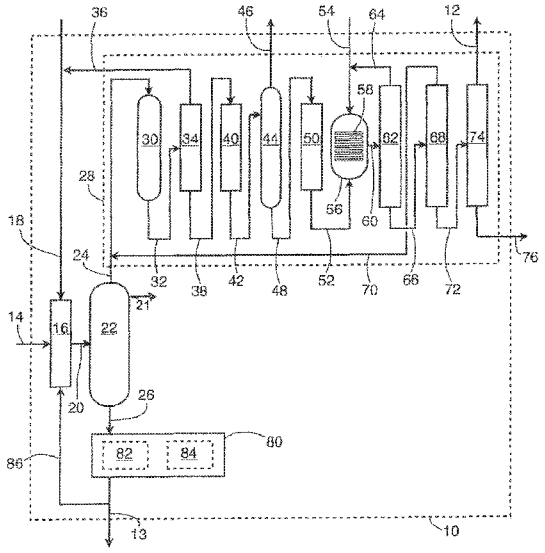


FIG. 1

WO 2014/200892 A1

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

LINEAR ALKYLBENZENES FROM NATURAL OILS AND METHODS OF PRODUCING

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 61/833,354 which was filed June 10, 2013, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates generally to alkylbenzenes from natural oils and methods for production of linear alkylbenzenes from natural oils. In an optional embodiment, biofuel may be co-produced with the renewable alkylbenzene.

BACKGROUND OF THE INVENTION

[0003] Linear alkylbenzenes are organic compounds with the formula $C_6H_5C_nH_{2n+1}$. While n can have any practical value, current commercial use of alkylbenzenes requires that n lie in the range of 10 to 16, or in the range of 8 to 15, or in the range of 10 to 13, or in the range of 12 to 15, or in the range of 9 to 14. These specific ranges are often required when the alkylbenzenes are used as intermediates in the production of surfactants for detergents. Because the surfactants created from alkylbenzenes are biodegradable, the production of alkylbenzenes has grown rapidly since their initial uses in detergent production in the 1960s. The linearity of the paraffin chain in the alkylbenzenes is key to the material's biodegradability and effectiveness as a detergent. A major factor in the final linearity of the alkylbenzenes is the linearity of the paraffin component

[0004] While detergents made utilizing alkylbenzene-based surfactants are biodegradable, processes for creating alkylbenzenes are not based on renewable sources. Specifically, alkylbenzenes are currently 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 may be support for using an alternate source for biodegradable surfactants in detergents and in other industries.

[0005] Accordingly, it is desirable to provide linear alkylbenzenes with a high degree of linearity and with an increased content of "new carbon" and methods and systems for producing the linear alkylbenzenes from natural oils, i.e., oils that are not extracted from the earth. Further, it is desirable to provide renewable linear alkylbenzenes from easily processed triglycerides and fatty acids from vegetable, animal, nut, and/or seed oils. Optionally, biofuels may be co-produced with the linear alkylbenzenes. 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 conjunction with the accompanying drawing and this background of the invention.

SUMMARY OF THE INVENTION

[0006] Methods for the co-production of an alkylbenzene product and biofuel from a natural oil are provided herein. In accordance with an exemplary embodiment, the method deoxygenates the natural oil to form a stream comprising paraffins. Then, a first portion of the paraffins are dehydrogenated to provide mono-olefins. In the method, the mono-olefins are used to alkylate benzene under alkylation conditions. As a result of alkylation, an alkylation effluent comprising alkylbenzenes and benzene is created. The alkylbenzenes are isolated from the effluent to provide the alkylbenzene product. A second portion of the paraffins is processed to form biofuel.

[0007] In another exemplary embodiment, a method is provided for the co-production of an alkylbenzene product and a biofuel from natural oil source triglycerides. In this embodiment, the triglycerides are deoxygenated to form a stream comprising water, carbon dioxide, carbon monoxide, propane, a first portion of paraffins, and a second portion of paraffins. This stream is fractionated to separate the first and second portions of paraffins. Then, the first portion of paraffins is dehydrogenated to provide mono-olefins. The mono-olefins are used to alkylate benzene under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene. Thereafter, alkylbenzenes are isolated to provide the alkylbenzene product. The second portion of paraffins is processed to form biofuel.

[0008] In accordance with another embodiment, a method for co-production of an alkylbenzene product and biofuel from natural oil is provided. In the method, the natural oil is deoxygenated with hydrogen to form a stream comprising paraffins. A first portion of the paraffins is dehydrogenated to provide mono-olefins and hydrogen. According to

the exemplary embodiment, the hydrogen provided by dehydrogenation is recycled to deoxygenate the natural oils. The mono-olefins are used to alkylate benzene under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene. Then, the alkylbenzenes are isolated from the effluent to provide the alkylbenzene product. A second portion of the paraffins is processed to form biofuel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Embodiments of the present invention will hereinafter be described in conjunction with the following drawing figure wherein:

[0010] FIG. 1 schematically illustrates a system for co-production of alkylbenzene and biofuel in accordance with an exemplary embodiment.

[0011] FIG. 2 is a plot of iso/normal ratio for C15-C18 carbon chain lengths versus hours on stream in accordance with Example 2.

[0012] FIG. 3 is a plot of the mass percent iso C15-C18 carbon chain lengths of all C15-C18 product versus temperature in accordance with Example 3.

DETAILED DESCRIPTION

[0013] 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.

[0014] As used in the present disclosure, the terms "renewably-based" or "renewable" denote that the carbon content of the renewable hydrocarbon (paraffins, olefins, aromatics, alkylbenzene, linear alkylbenzene or subsequent products prepared from renewable hydrocarbons), is from a "new carbon" source as measured by ASTM test method D6866-05, "Determining the Bio-based Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis", hereby incorporated by reference in its entirety. This test method measures the $^{14}C/^{12}C$ isotope ratio in a sample and compares it to the $^{14}C/^{12}C$ isotope ratio in a standard 100 mass % bio-based material to give percent bio-based content of the sample. Additionally, "Bio-based materials" are organic materials in which the carbon comes from recently, on a human time scale, fixated CO_2 present in the atmosphere using sunlight energy, photosynthesis. On land, this CO_2 is captured or fixated by plant life such as agricultural crops or forestry materials. In the oceans, the CO_2

is captured or fixated by photosynthesizing bacteria or phytoplankton. For example, a bio-based material has a $^{14}C/^{12}C$ isotope ratio greater than 0. Contrarily, a fossil-based material has a $^{14}C/^{12}C$ isotope ratio of 0. The term "renewable" with regard to compounds such as hydrocarbons (paraffins, olefins, di-olefins, aromatics, alkylbenzene, linear alkylbenzene etc.) also refers to compounds prepared from biomass using thermochemical methods such as (e. g., Fischer-Tropsch catalysts), biocatalysts (e. g., fermentation), or other processes, for example.

[0015] A small amount of the carbon atoms in the atmospheric carbon dioxide is the radioactive isotope ^{14}C. This ^{14}C carbon dioxide is created when atmospheric nitrogen is struck by a cosmic ray generated neutron, causing the nitrogen to lose a proton and form carbon of atomic mass 14 (^{14}C), which is then immediately oxidized, to carbon dioxide. A small but measurable fraction of atmospheric carbon is present in the form of ^{14}C. Atmospheric carbon dioxide is processed by green plants to make organic molecules during the process known as photosynthesis. Virtually all forms of life on Earth depend on this green plant production of organic molecules to produce the chemical energy that facilitates growth and reproduction. Therefore, the ^{14}C that forms in the atmosphere eventually becomes part of all life forms and their biological products, enriching biomass and organisms which feed on biomass with ^{14}C. In contrast, carbon from fossil fuels does not have the signature $^{14}C/^{12}C$ ratio of renewable organic molecules derived from atmospheric carbon dioxide. Furthermore, renewable organic molecules that biodegrade to CO_2 do not contribute to an increase in atmospheric greenhouse gases as there is no net increase of carbon emitted to the atmosphere.

[0016] Assessment of the renewably based carbon content of a material can be performed through standard test methods such as using radiocarbon and isotope ratio mass spectrometry analysis. ASTM International (formally known as the American Society for Testing and Materials) has established a standard method for assessing the bio-based content of materials. The ASTM method is designated ASTM-D6866.

[0017] The application of ASTM-D6866 to derive "biobased content" is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (^{14}C) in an unknown sample compared to that of a modern reference standard. This ratio is reported as a percentage with the units "pMC" (percent modern carbon). If the material being analyzed is a mixture

of present day radiocarbon and fossil carbon, which contains very low levels of radiocarbon, then the pMC value obtained correlates directly to the amount of biomass material present in the sample.

[0018] A renewable linear alkylbenzene product is provided which has the general chemical formula $C_6H_5C_nH_{2n+1}$ of which the carbon is predominantly modern carbon, as defined and measured by ASTM D6866, and not derived from petroleum, and has a linearity of the paraffin alkyl group preferably of greater than 80 mass % but more preferably greater than 90 mass % and most preferably of at least 92 mass%. Thus the alkylbenzene product contains at least 80 mass % of linear alkylbenzenes meaning alkylbenzenes wherein the paraffin alkyl group is a linear paraffin alkyl group. The renewable linear alkylbenzene consists of a benzene ring which comprises the portion of the chemical formula of C_6H_5 that is alkylated with linear paraffin which is described by the C_nH_{2n+1} portion of the formula. Often, linear alkylbenzenes are sulfonated to produce a linear alkylbenzene sulfonate as a surfactant for use in detergents. For the purposes of use as material to produce a linear alkyl benzene sulfonate it is preferable that the paraffins carbon chain length (n in the chemical formula) of the alkyl group is in the range of 10 to 16, or in the range of 8 to 15, or in the range of 10 to 13, or in the range of 12 to 15, or in the range of 9 to 14. The carbons on the paraffin chain will be rich in carbon-14 isotope relative to that seen in petroleum derived paraffins. Carbon enriched in carbon-14 isotope is generally considered modern carbon, atmospheric carbon, or new carbon and is an indicator of how much renewable carbon is in the compound. Analytical methods such as ASTM D6866, as discussed above, can be used to determine the amount of carbon content that is modern carbon and not derived from petroleum by analyzing the amount of carbon-14 isotope in the compound. In one embodiment, the renewable linear alkylbenzene is at least 5 mass % modern carbon, in another embodiment more than 10 mass % modern carbon, in another embodiment more than 30 mass % modern carbon, and yet another embodiment more than 50 mass % modern carbon and still another embodiment greater than 60 mass % modern carbon.

[0019] The linearity of alkylbenzene product is mostly dependent on the linearity of the paraffins used to alkylate the benzene. It is a common rule of thumb by those skilled in the art that the linearity of a paraffin feed drops by 5-7 mass % after dehydrogenation and alkylation. Therefore paraffin with 97 mass % linearity (or alternatively 3 mass %

isoparaffin) would result in an alkylbenzene product with linearity around 90-92 mass %. This sets the requirement for paraffin linearity 5-7 mass % higher than the specification for the alkylbenzene product. Typically the linearity of the paraffin product is measured by UOP 621, UOP 411, or UOP 732, which are standard test methods available from ASTM, which are hereby incorporated by reference in their entirety. Linear alkylbenzenes may be analyzed using ASTM Standard Test Method D4337 hereby incorporated by reference in its entirety.

[0020] Contrary to current theory, hydrocracking to a lower carbon chain length from a longer chain length is a very inefficient way to produce normal paraffins. For example, most plant oils have predominantly C16 and C18 carbon chains. If C10 to C13 carbon chains are required to make the desired alkylbenzene product, one might believe that cracking the hydrodeoxygenated C16 and C18 n-paraffins and the decarboxylated/decarbonylated C15 and C17 n-paraffins to the C10 to C13 range would be a suitable route. However, hydrocracking results in almost exclusively branched paraffins so very little of a hydrocracked product material would result in normal paraffins. Therefore to produce linear paraffins in the interesting carbon number ranges for linear alkyl benzene it is highly preferable to use oil with large amounts of C10, C12 and C14 carbon chain length fatty acids, these oils include coconut oil, palm kernel oil and babassu oil.

[0021] Alternatively, other natural oils may be used in the feedstock when the amount of nitrogen contained in components of the feedstock is low, such as less than 3 wt. ppm nitrogen, as shown in Examples 3 and 4, and or when the temperature for the deoxygenation is maintained below the temperature needed for hydrocracking or isomerization. Concentrations of nitrogen in nitrogen containing compounds as discussed herein refer to the amount of elemental nitrogen in a compound as measured by, for example, chemiluminescence techniques such as UOP Method 981 available from ASTM. PPM values are by weight unless stated otherwise. In addition, purification steps may be applied to feedstocks to adjust the nitrogen content to less than 3 wt. ppm nitrogen. Another technique to control the linearity of the paraffins produced is to control the temperature in the deoxygenation zone to a temperature less than that effective for isomerization or hydrocracking. In these embodiments, suitable natural oil feedstocks include those derived from plant or algae matter, and are often referred to as renewable

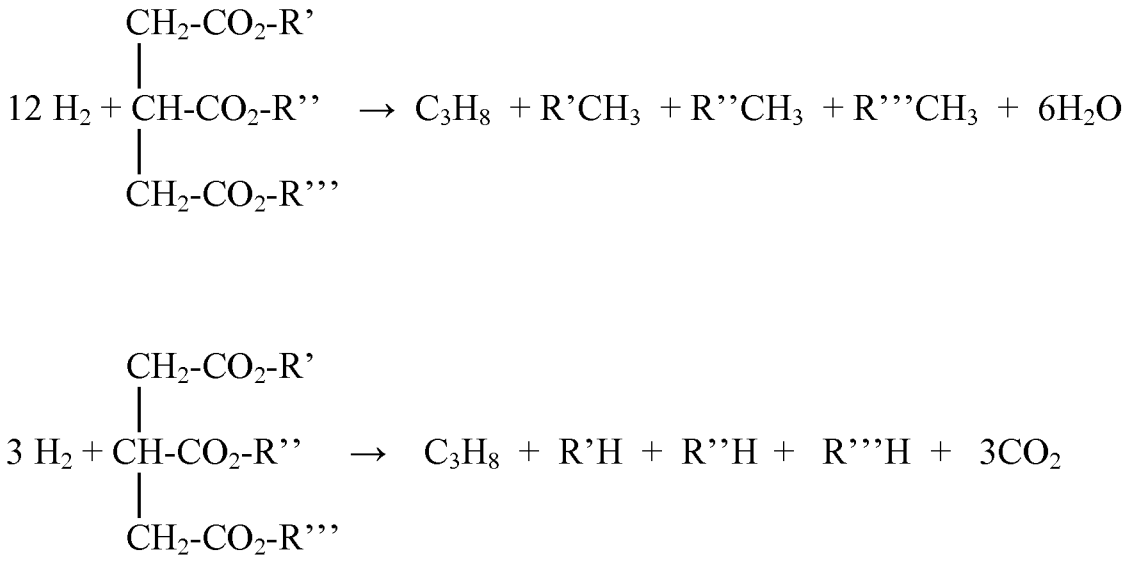
oils. Natural oils are not based on kerosene or other fossil fuels. In certain embodiments, the natural oils include one or more of coconut oil, babassu oil, palm kernel oil, castor oil, cooking oil, and other vegetable, nut or seed oils. The natural oils typically comprise triglycerides, free fatty acids, or a combination of triglycerides and free fatty acids.

[0022] Various embodiments contemplated herein relate to methods and systems for producing an alkylbenzene product from specific natural oils. In FIG. 1, an exemplary system 10 for producing an alkylbenzene product 12 from a specific natural oil feed 14 is illustrated. In one specific embodiment, a portion of the paraffins generated by the dehydrogenating step may be processed to co-produce a bio fuel, and FIG. 1 also shows this optional embodiment where a portion of the paraffins generated by the dehydrogenating step are used to produce biofuel 13. The natural oil feed is selected from the group consisting of coconut oil, palm kernel oil, babassu oil, and mixtures thereof. Natural oils are not based on kerosene or other fossil fuels. The natural oils comprise triglycerides, free fatty acids, or a combination of triglycerides and free fatty acids.

[0023] In the illustrated embodiment, the natural oil feed 14, which is selected from the group consisting of palm kernel oil, coconut oil, babassu oil and mixtures thereof, is delivered to a deoxygenation unit 16 which also receives a hydrogen feed 18. In the deoxygenation unit 16, the triglycerides and fatty acids in the feed 14 are deoxygenated and converted into normal paraffins. 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 normal paraffins. The glycerol is converted into propane, and the oxygen in the hydroxyl and carboxyl groups is converted into water, carbon dioxide, or carbon monoxide. The deoxygenation reaction for fatty acids and triglycerides are respectively illustrated as:

$$3H_2 + RCOOH \rightarrow RCH_3 + 2H_2O$$

$$RCOOH \rightarrow RH + CO_2$$



During the deoxygenation reaction, the length of a paraffin chain R^n created will vary by a value of one depending on the exact reaction pathway. It is understood that deoxygenation includes at least one of hydrodeoxygenation, decarboxylation, and decarbonylation, or any combination thereof. For instance, if carbon dioxide is formed, then the chain will have one fewer carbon than the fatty acid source. If water is formed, then the chain will match the length of in the fatty acid source. With these feed materials, many of the paraffins produced have even numbers of carbon atoms as shown in Example 1.

[0024] Operating conditions for the deoxygenating unit include pressures in the range of from 250 to 800 psig (1724 to 5516 kPa) and temperatures in the range of from 525°F to 700°F (274°C to 371°C) in one embodiment, from 525°F to 640°F (274°C to 338°C) in another embodiment and from 525°F to 590°F (274°C to 310°C) in another embodiment. Catalysts may include those containing one or more of Ni, Mo, Co, P, such as Ni-Mo, Ni-Mo-P, Ni-Co-Mo, or Co-Mo, on aluminas, silica, titania, zirconia, and mixtures thereof. Suitable hydrogen to hydrocarbon ratios include from 1500 to 8000, from 3500 to 7600, and from 3500-6000 standard cubic feet per barrel of feedstock (scf/B). Suitable space velocities include 0.2 – 3.0 hr^{-1} LHSV. Conditions are selected to minimize cracking or isomerizing the paraffins.

[0025] In FIG. 1, a deoxygenated stream 20 containing normal paraffins, water, carbon dioxide, carbon monoxide, and propane exits the deoxygenation unit 16 and is fed to a

separator 22. The separator 22 may be a multi-stage fractionation unit, distillation system or similar known apparatus. In any event, the separator 22 removes the water, carbon dioxide, carbon monoxide, and propane (stream 21) from the deoxygenated stream 20. Further, the separator 22 may provide a first portion of paraffins 24 and a second portion of paraffins 26. In certain embodiments, the first portion of paraffins 24 has carbon chain lengths of C_{10} to C_{14}. In other embodiments, the first portion of paraffins 24 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 optional second portion of paraffins 26 may have carbon chains shorter than, longer than, or a combination of shorter and longer than, the chains of the first portion of paraffins 24. In a specific embodiment, the first portion of paraffins 24 comprises paraffins with C_{10} to C_{13} chains and the optional second portion of paraffins 26 comprises paraffins with C_{14} to C_{18} chains.

[0026] As shown in FIG. 1, the first portion of paraffins 24 is introduced to an alkylbenzene production zone 28. Specifically, the first portion of paraffins 24 is fed into a dehydrogenation unit 30 in the alkylbenzene production unit 28. In the dehydrogenation unit 30, the first portion of paraffins 24 are dehydrogenated into mono-olefins of the same carbon numbers as the first portion of paraffins 24. Typically, dehydrogenation occurs through known catalytic processes, such as the commercially popular Pacol process. Di-olefins (i.e., dienes) and aromatics are also produced as an undesired result of the dehydrogenation reactions as expressed in the following equations:

Mono-olefin formation: $C_XH_{2X+2} \rightarrow C_XH_{2X} + H_2$

Di-olefin formation: $C_XH_{2X} \rightarrow C_XH_{2X-2} + H_2$

Aromatic formation: $C_XH_{2X-2} \rightarrow C_XH_{2X-6} + 2H_2$

[0027] Operating conditions for the dehydrogenation unit include space velocities from 5 to 50 hr^{-1} LHSV and from 20 to 32 hr^{-1} LHSV; pressures from 5 psig to 50 psig and from 15 psig; to 25 psig; temperatures from 400°C – 500°C and from 440°C to 490°C, and hydrogen to hydrocarbon mole ratios from 1 – 12 and from 3-7. An example of a suitable catalyst is a Pt on alumina catalyst where platinum is attenuated with an attenuator metal.

Another suitable catalyst is described in US 6,177,381 hereby incorporated by reference. The unit may be operated dry or with water injection up to 2000 mass-ppm water.

[0028] In FIG. 1, a dehydrogenated stream 32 exits the dehydrogenation unit 30 comprising mono-olefins and hydrogen, as well as some di-olefins and aromatics. The dehydrogenated stream 32 is delivered to a phase separator 34 for removing the hydrogen from the dehydrogenated stream 32. As shown, the hydrogen exits the phase separator 34 in a recycle stream of hydrogen 36 that can be added to the hydrogen feed 18 to support the deoxygenation process upstream.

[0029] At the phase separator 34, a liquid stream 38 is formed and comprises the mono-olefins 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, such as a DeFine reactor. 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.

[0030] As shown, the enhanced stream 42 passes from the hydrogenation unit 40 to a lights separator 44, such as a stripper column, which removes a light end stream 46 containing any lights, such as butane, propane, ethane and methane, that resulted from cracking or other reactions during upstream processing. With the light ends 46 removed, stream 48 is formed and may be delivered to an aromatic removal apparatus 50, such as a Pacol Enhancement Process (PEP) unit available from UOP. As indicated by its name, the aromatic removal apparatus 50 removes aromatics from the stream 48 and forms a stream of mono-olefins 52.

[0031] In FIG. 1, 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. Fluorided silica-alumina, hydrogen fluoride (HF), aluminum chloride ($AlCl_3$), and zeolitic catalysts are examples of major catalysts in commercial use for the alkylation of benzene with linear mono-olefins and may be used in the alkylation unit 56. As a result of alkylation, alkylbenzene, typically called linear alkylbenzene (LAB), is formed according to the reaction:

$$C_6H_6 + C_XH_{2X} \rightarrow C_6H_5C_XH_{2X+1}$$

and are present in an alkylation effluent 60.

[0032] Suitable operating conditions for the alkylation unit include space velocities from 1 to 10 hr^{-1} LHSV, pressures to maintain liquid phase operation such as 300 to 600 psig, temperatures in the range of from 80°C to 180°C and 120°C to 170°C, benzene to olefin mole ratios of 3 to 40 and 8 to 35.

[0033] Surplus amounts of benzene 54 are supplied to the alkylation unit 56 to achieve high degree of desired alkylation. 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. 1, 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.

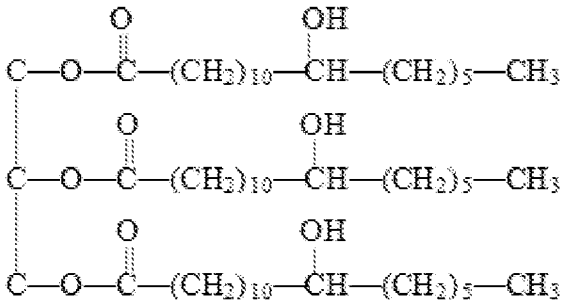
[0034] As shown, a benzene-stripped stream 66 exits the benzene separation unit 62 and enters a paraffinic separation unit 68, such as a fractionation column. In the paraffinic separation unit 68, unreacted paraffins are removed from the benzene-stripped stream 66 in a recycle paraffin stream 70, and are routed to and mixed with the first portion of paraffins 24 before dehydrogenation as described above.

[0035] 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.

[0036] As a result of the post-alkylation separation processes, the linear alkylbenzene product 12 is isolated and exits the apparatus 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 14 may be of sufficient quality that no fractionation is necessary despite the desired chain length

range. In certain embodiments, the feed 14 is substantially homogeneous and comprises free fatty acids within a desired range. For instance, the feed may be entirely Lauric free fatty acid such that all the free fatty acids of the feed have 12 carbon atoms. Alternatively, the feed 14 may comprise triglycerides and free fatty acids that all have carbon chain lengths appropriate for a desired alkylbenzene product 12.

[0037] In certain embodiments, the natural oil source is castor, and the feed 14 comprises castor oils. Castor oils consist essentially of C_{18} fatty acids with an additional, internal hydroxyl groups at the carbon-12 position. For instance, the structure of a castor oil triglyceride is:



During deoxygenation of a feed 14 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 C_{10} to C_{11} chains resulting from cleavage during deoxygenation, and a group of non-cleaved heavier paraffins having C_{17} to C_{18} chains. The lighter paraffins may form the first portion of paraffins 24 and the heavier paraffins may form the second portion of paraffins 26. 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. Another embodiment may involve a pathway such as found in USAN 13/712181. As such, any oil with an internal hydroxyl group may be a desirable feed oil. Also, it may be desirable to modify regular vegetable oils, such as soybean or jatropha oil such that they contain internal hydroxyl groups, similar to the structure of castor oil, and thus the modified oil would behave similarly to castor oil upon deoxygenation, producing a first and second portion of paraffins. Examples of such modifications are described in USAN 13/712,181 hereby incorporated by reference in its entirety

[0038] The second portion of paraffins 26 may be recovered or may be further processed. As shown in FIG. 1, the second portion of paraffins 26 may be optionally fed to

a system 80 for producing biofuel 13 such as diesel or jet fuel. Typically, no further deoxygenation is needed in the biofuel production system 80. Rather, in the system 80, the second portion of paraffins 26 are typically isomerized in an isomerization unit 82 or cracked in a cracking unit 84 to create the isoparaffins of equal or lighter molecular weight than the second portion of paraffins 26. Hydrogen not consumed during these processes is separated out from the resulting biofuel 13 to form a hydrogen stream 86 that is recycled to the deoxygenation unit 16. While shown feeding the deoxygenation unit 16 directly, the hydrogen stream 86 could be fed to hydrogen feed 18.

[0039] In order to create green diesel, the biofuel production system 80 primarily isomerizes the second portion of paraffins 26 with minimal cracking. For the production of biojet or green jet fuel, some cracking is performed in order to obtain smaller molecules (with reduced molecular weight) to meet the more stringent freeze points required by jet specifications.

[0040] 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.

[0041] The product produced herein is a linear alkylbenzene product comprising: alkylbenzenes having the formula $C_6H_5C_nH_{2n+1}$ wherein n is from 12 to 13; wherein the alkylbenzenes have at least 7 mass % modern carbon as measured by ASTM Method 6866; and wherein at least 80 mass % of the alkylbenzenes having the formula $C_6H_5C_nH_{2n+1}$ wherein n is from 12 to 13, have linear alkyl groups. In other words, linear alkyl groups are present in at least 80 mass% of the alkylbenzenes produced where the alkylbenzenes have the formula $C_6H_5C_nH_{2n+1}$ wherein n is from 12 to 13. In other embodiments at least 90 mass % of the alkylbenzenes have linear alkyl groups or at least 91 mass % of the alkylbenzenes have linear alkyl groups. In other embodiments the alkylbenzenes have at least 10 mass % modern carbon, 30 mass % modern carbon, 50 mass % modern carbon or

60 mass % modern carbon as measured by ASTM Method 6866. In other embodiments, n is from 12 to 15, or n is from 10-13 or n is from 10 to 16.

[0042] The linear alkylbenzene may be sulfonated to provide a linear alkylbenzene sulfonate product comprising: alkylbenzene sulfonate compounds having the formula $C_nH_{2n+1}C_6H_4SO_3H$ wherein n is from 12 to 13; wherein the alkylbenzene sulfonate compounds have at least 5 mass % modern carbon as measured by ASTM Method 6866; wherein the alkyl group is a linear alkyl group for at least 80 mass % of the alkylbenzene sulfonate compounds having the formula $C_nH_{2n+1}C_6H_4SO_3H$ wherein n is from 12 to 13. In other embodiments alkyl group is a linear alkyl group for at least 90 mass % of the linear alkylbenzene sulfonates have linear alkyl groups or at least 91 mass % of the linear alkylbenzene sulfonates. In other embodiments the linear alkylbenzene sulfonate has at least 10 mass % modern carbon, or 30 mass % modern carbon, or 50 mass % modern carbon, or 60 mass % modern carbon as measured by ASTM Method 6866. In other embodiments, n is from 12 to 15, or n is from 10-13, or n is from 10 to 16.

Example 1

[0043] Coconut oil was deoxygenated to produce paraffins which were then used in the production of renewable linear alkylbenzene. During this operation paraffins were produced with different degrees of linearity. The deoxygenation was performed over a Ni-Mo catalyst supported on alumina. As can be seen in Table 1 with fully active catalyst much isomerization is apparent. After the catalyst is attenuated it loses it isomerization activity and high linearity is obtained. Commensurate with that decarboxylation activity is lost and as shown by the ever increasing even to odd carbon number ratio with time which also increases with increasing carbon number. It is surprising that the odd numbered carbon chain lengths increase relative to the even with increasing carbon number. This indicates that higher carbon chain length oils would provide a smoother carbon chain distribution than lower carbon number chain lengths.

Table 1

Hours on stream	21	42	74	94	118
Temperature (F)	594	615	612	612	621
Pressure (psig)	600	600	600	600	600
LHSV (hr-1)	0.72	1	1	1	1
H2:HC (SCFB)	5277	3800	3800	3800	3800
Iso% by C#					
Ratio of isoparaffins between subject n-paraffin to next lightest n-paraffin					
Isos between nC8 and nC9/nC9	26.9%	4.2%	2.1%	2.4%	2.7%
Isos between nC9 and nC10/nC10	7.8%	1.2%	0.9%	1.1%	1.4%
Isos between nC10 and nC11/nC11	4.7%	0.6%	0.6%	0.6%	1.0%
Isos between nC11 and nC12/nC12	1.6%	0.8%	0.7%	0.7%	0.9%
Isos between nC12 and nC13/nC13	6.0%	1.2%	1.1%	1.2%	1.7%
Isos between nC13 and nC14/nC14	2.2%	1.0%	0.7%	0.8%	1.0%
Isos > nC14/nC14+	4.1%	0.4%	0.4%	0.5%	0.6%

Example 2

[0044] A Ni-Mo catalyst was used to deoxygenate soybean oil. As shown in FIG. 2, while the isomerization activity was still high at the beginning of the run the linearity suffered. However, with time and this particular catalyst the isomerization activity decreased providing adequate linearity for the paraffin product to be used as a linear alkylbenzene precursor. The soybean oil is almost entirely composed of C16 and C18 fatty acid chains, so no subsequent cracking to shorten the resulting paraffins is required. Due to the clean nature of the feed, less than 2 wt. ppm nitrogen, the reactor could be run at a low temperature avoiding reaching isomerization activation temperature.

Example 3

[0045] A more difficult to treat feedstock was run over two beds of Ni-Mo catalyst on alumina at a total LHSV of 0.33 hr^{-1}. The feed contained over 100 wt-ppm nitrogen. The feed was diluted 2:1 diluent:feed and run at elevated temperature to overcome the deoxygenation inhibition from the nitrogen. As shown in FIG. 3 the iso content of paraffins at the elevated operating temperatures resulted in at least 3.5 mass % non-linear paraffin, less than 96.5 mass % linearity, and increased with increasing temperature to 6 mass % as the catalyst deactivated and higher temperatures were required.

Example 4

[0046] Various deoxygenations at commercial scale, 250 bpd feed rate, were carried out on a variety of oils. The composite of these large scale runs shows a similar trend of nitrogen content of the feedstock versus isomerization of the generated paraffin and loss of linearity, see Table 2. The low nitrogen containing feeds, from palm and soy bean oil had iso/normal weight ratios of less than 0.1 while oils from higher nitrogen containing feedstocks from jatropha and camelina seed had iso/normal ratios greater than 0.1. For oils with naturally occurring high nitrogen content, refining the oil can reduce the nitrogen content to make it more suitable for highly linear paraffin production. Refining of the oil can reduce the nitrogen to make it more suitable for highly linear paraffin production.

Table 2

	Jatropha1	Jatropha2	Camelina1	Camelina2	Palm	Soy
C14-C22 Iso: Normal Ratio	0.17	0.19	0.12	0.19	0.04	0.07
Typical Feed Nitrogen Content (wt-ppm)	18-31	18-31	9	9	3	<1

Example 5

[0047] A coconut oil feed was deoxygenated, to form paraffins, dehydrogenated to form mono-olefins, and benzene was alkylated with the mono-olefins to form an alkylbenzene product with a modern carbon content of 62 mass% modern carbon as determined by ASTM D6866 as compared to a theoretical modern carbon content of 66.4 mass %, a bromine number of 1 g Br/per gram sample as determined by UOP standard test method 304, incorporated by reference, and a linearity of 92 mass %.

SPECIFIC EMBODIMENTS

[0048] 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.

[0049] A first embodiment of the invention is a method for generating an alkylbenzene product from a natural oil comprising deoxygenating feedstock comprising natural oil having less than 3 wt. ppm of nitrogen contained in nitrogen containing compounds to form a stream comprising paraffins; dehydrogenating at least a portion of the paraffins to provide mono-olefins; alkylating benzene with the mono-olefins under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene;

separating the alkylbenzenes to provide the alkylbenzene product comprising alkylbenzenes having an alkyl group of n carbon atoms where n is from 12 to 13 and wherein the alkyl group is a linear alkyl group for at least 80 mass % of the alkylbenzenes having an alkyl group of n carbon atoms. The alkylbenzene product produced by the method of the first embodiment above. 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, sulfonating the alkylbenzene product to form a linear alkylbenzene sulfonate product. The linear alkylbenzene sulfonate product produced by the method of the preceding embodiment. 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 where n is expanded to include from 8 to 15. 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 where n is expanded to include from 10 to 13. 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 where n is expanded to include from 9 to 14. 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 a hydrogen stream results from dehydrogenating the paraffins, and wherein the method further comprises recycling the hydrogen stream to the deoxygenating step. 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 a second portion of paraffins from the stream comprising paraffins, and isomerizing the second portion of paraffins to form isoparaffins. 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 di-olefins are also generated by dehydrogenating the paraffins, and wherein the method further comprises selectively hydrogenating the di-olefins to form additional mono-olefins. 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 aromatics are also generated by dehydrogenating the paraffins, the method further comprising removing aromatics from the mono-olefins before alkylating. 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 the deoxygenating utilizes a catalyst

comprising a component selected from the group consisting of Ni , Mo, Co, P, and mixtures thereof. 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 the deoxygenating utilizes a catalyst comprising a component selected from the group consisting of aluminas, silica, titania, zirconia, and mixtures thereof. 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 wherein the deoxygenating utilizes a catalyst comprising a first component selected from the group consisting of Ni , Mo, Co, P, and mixtures thereof and a second component selected from the group consisting of aluminas, silica, titania, zirconia, and mixtures thereof. 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 wherein the deoxygenating utilizes a catalyst comprising a first component selected from the group consisting of Ni-Mo, Ni-Mo-P, Ni-Co-Mo, and Co-Mo and a second component selected from the group consisting of aluminas, titania, zirconia, and mixtures thereof.

[0050] A second embodiment of the invention is a method of increasing the amount of modern carbon in detergents comprising deoxygenating feedstock comprising natural oil having less than 3 wt. ppm nitrogen, the nitrogen contained in nitrogen containing compounds as measured by UOP Method 981, to form a stream comprising paraffins wherein the paraffins have at least 7 mass % modern carbon; dehydrogenating at least a portion of the paraffins having at least 7 mass % modern carbon to provide mono-olefins; alkylating benzene with the mono-olefins under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene; separating the alkylbenzenes to provide the alkylbenzene product comprising alkylbenzenes having an alkyl group having n carbon atoms where n is from 12 to 13 and wherein the alkyl group is a linear alkyl group for at least 80 mass % of the alkylbenzenes having an alkyl group of n carbon atoms; sulfonating the alkylbenzene product to form linear alkylbenzene sulfonate; and adding the linear alkylbenzene sulfonate to a detergent formulation. 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 where n is expanded to include from 8 to 15. 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

where n is expanded to include from 10 to 13. 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 where n is expanded to include from 9 to 14. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the stream comprising paraffins has at least 10 mass % modern carbon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the stream comprising paraffins has at least 30 mass % modern carbon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the stream comprising paraffins has at least 50 mass % modern carbon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the stream comprising paraffins has at least 60 mass % modern carbon.

[0051] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0052] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS

What is claimed is:

1. A method for generating an alkylbenzene product from a natural oil comprising:

deoxygenating feedstock comprising natural oil having less than 3 wt. ppm of nitrogen contained in nitrogen containing compounds to form a stream comprising paraffins;

dehydrogenating at least a portion of the paraffins to provide mono-olefins;

alkylating benzene with the mono-olefins under alkylation conditions to provide an alkylation effluent comprising alkylbenzenes and benzene;

separating the alkylbenzenes to provide the alkylbenzene product comprising alkylbenzenes having an alkyl group of n carbon atoms where n is from 12 to 13 and wherein for at least 80 mass % of the alkylbenzenes having an alkyl group of n carbon atoms the alkyl group is linear.

2. The method of 1 further comprising, sulfonating the alkylbenzene product to form a linear alkylbenzene sulfonate product.

3. The linear alkylbenzene sulfonate product produced by the method of claim 3.

4. The method of claim 1 wherein a hydrogen stream results from dehydrogenating the paraffins, and wherein the method further comprises recycling the hydrogen stream to the deoxygenating step.

5. The method of claim 1 further comprising separating a second portion of paraffins from the stream comprising paraffins, and isomerizing the second portion of paraffins to form isoparaffins.

6. The method of claim 1 wherein di-olefins are also generated by dehydrogenating the paraffins, and wherein the method further comprises selectively hydrogenating the di-olefins to form additional mono-olefins.

7. The method of claim 1 wherein aromatics are also generated by dehydrogenating the paraffins, the method further comprising removing aromatics from the mono-olefins before alkylating.

8. The method of claim 1 wherein the deoxygenating utilizes a catalyst comprising a component selected from the group consisting of Ni , Mo, Co, P, and mixtures thereof.

9. The method of claim 1 wherein the deoxygenating utilizes a catalyst comprising a component selected from the group consisting of aluminas, silicas, titania, zirconia, and mixtures thereof.

10. The method of claim 2 further comprising adding the linear alkylbenzene sulfonate to a detergent formulation.

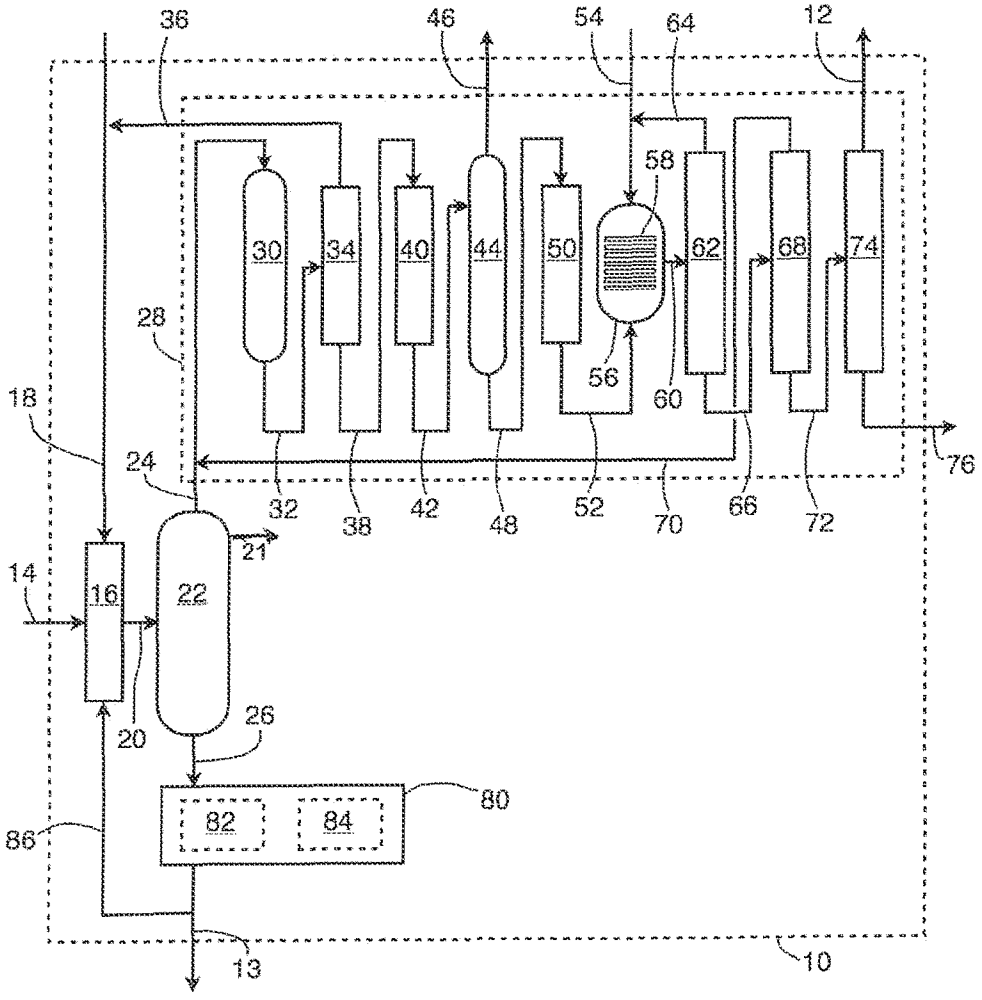

36
46
54
64
12
58
30
34
40
44
50
62
68
74
28
56
60
18
24
76
32
38
42
48
52
70
66
72
21
14
16
22
20
26
80
82
84
86
13
10

FIG. 1

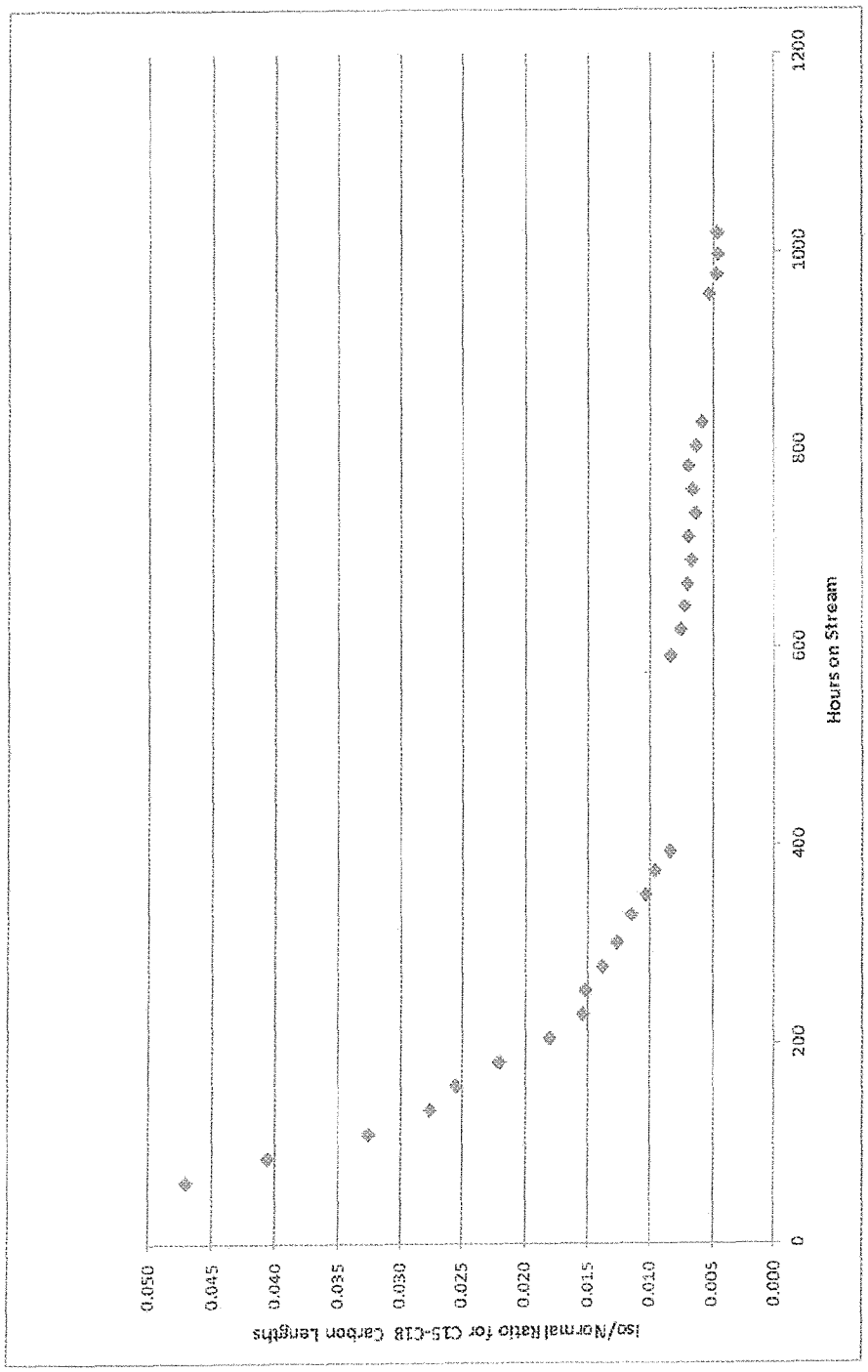

Iso/Normal Ratio for C15-C18 Carbon Lengths
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
200
400
600
800
1000
1200
Hours on Stream

FIG. 2

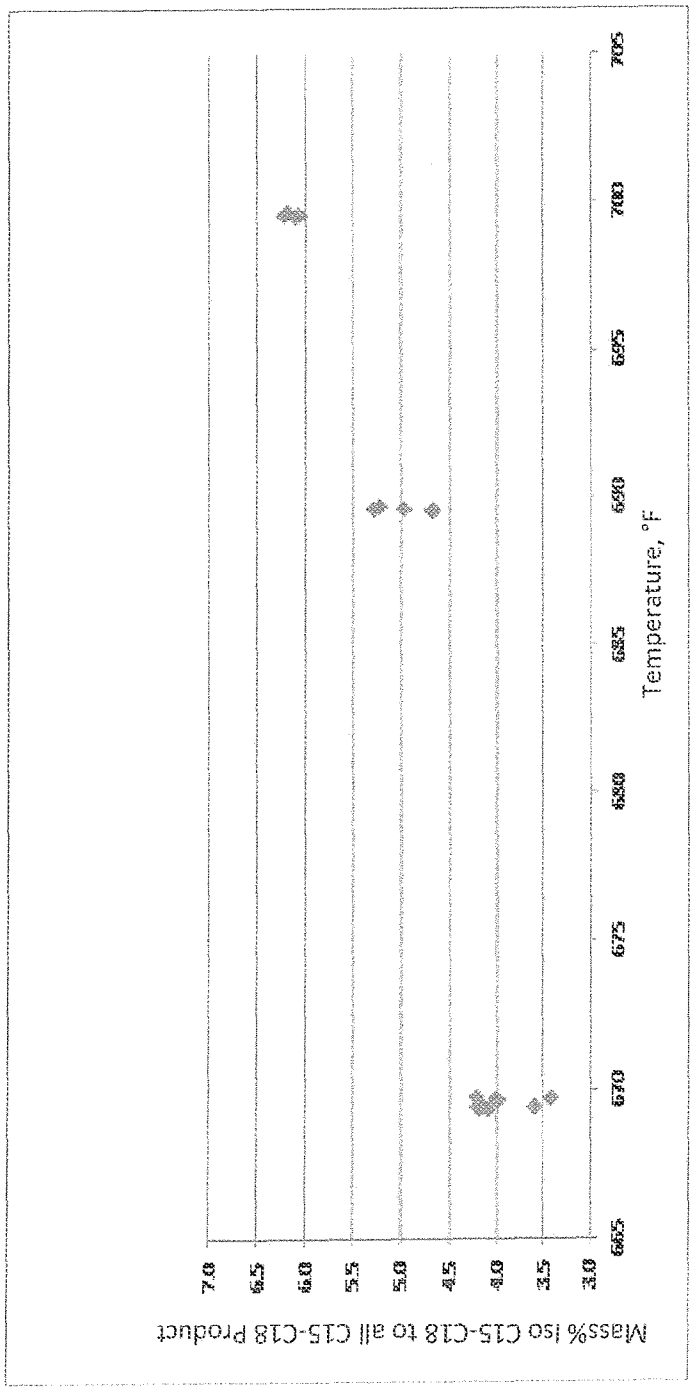

Mass% Iso C15-C18 to all C15-C18 Product
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
665
670
675
680
685
690
695
700
705
Temperature, °F

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/041494

A. CLASSIFICATION OF SUBJECT MATTER

C07C 7/00(2006.01)i, C07C 7/20(2006.01)i, C07C 2/58(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 7/00; C07C 1/207; C07C 2/66; B01F 7/26; C10G 45/00; C07C 7/20; C07C 2/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:linear alkylation, natural oil, deoxygenation, dehydrogenation, alkylation, separation, nitrogen content

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013-0079573 A1 (ANDREA G. BOZZANO et al.) 28 March 2013 See the abstract; paragraphs [0015], [0020]; and claims 1-20.	1,4-7
Y		2,3,8-10
Y	US 2004-0164000 A1 (ARMEN N. ABAZAJIAN) 26 August 2004 See the abstract; paragraphs [0031]-[0032], [0051]; and claims 1-56.	2,3,10
Y	KUBICKA D. et al., "Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts" Applied Catalysis A: General, 2010, Vol. 372, pp.199-208 See the abstract; and Figures 1-11.	8,9
A	WO 2009-003051 A2 (H R D CORPORATION et al.) 31 December 2008 See the abstract.	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent 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
"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
"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	Date of mailing of the international search report
08 October 2014 (08.10.2014)	**08 October 2014 (08.10.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
KIM, Jong Ho
Telephone No. +042 481 8657

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/041494

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013-0079573 A1	28/03/2013	CN 103827060 A	28/05/2014
		EP 2758360 A1	30/07/2014
		KR 10-2014-0061542 A	21/05/2014
		TW 201313891 A	01/04/2013
		US 8546629 B2	01/10/2013
		WO 2013-043279 A1	28/03/2013
US 2004-0164000 A1	26/08/2004	US 7311815 B2	25/12/2007
WO 2009-003051 A2	31/12/2008	CA 2689517 A1	31/12/2008
		CA 2689517 C	20/11/2012
		CN 101687727 A	31/03/2010
		CN 101687727 B	18/12/2013
		EA 200901413 A1	30/04/2010
		EP 2158173 A2	03/03/2010
		EP 2158173 A4	18/05/2011
		US 2009-0005622 A1	01/01/2009
		US 2010-0266465 A1	21/10/2010
		US 2012-296144 A1	22/11/2012
		US 8133447 B2	13/03/2012
		US 8278494 B2	02/10/2012
		US 8455706 B2	04/06/2013
		WO 2009-003051 A3	12/03/2009