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(54) Title: HETEROGENEOUS CATALYSTS FOR ISOMERIZING TERMINAL OLEFINS TO INTERNAL OLEFINS AND ASSOCIATED LINEAR INTERNAL OLEFIN COMPOSITIONS

(57) Abstract: Terminal olefins (alpha olefins) may be isomerized to internal olefins using a catalyst composition comprising sodium oxide on a solid support. Isomerization of alpha olefins takes place under a variety of mild heterogeneous reaction conditions. Linear alpha olefins (LAOs) may be isomerized without substantial cracking or branching to form the corresponding linear internal olefins (LIOs). The LIOs may be incorporated in drilling fluids, particularly those intended for use in a subsea environment, due to their favorable environmental profile and low pour point values. Compositions comprising C_{14}-C_{20} LIOs produced from the corresponding C_{14}-C_{20} LAOs may exhibit anaerobic biodegradability and pour point values of about -6°C or lower.

HETEROGENEOUS CATALYSTS FOR ISOMERIZING TERMINAL OLEFINS TO INTERNAL OLEFINS AND ASSOCIATED LINEAR INTERNAL OLEFIN COMPOSITIONS

PRIORITY

[0001] This application claims priority to Provisional Application No. 62/694,210, filed, July 5, 2019, the disclosure of which is incorporated herein by reference.

FIELD

[0002] The present disclosure relates to olefin isomerization using heterogeneous catalysts.

BACKGROUND

[0003] Linear alpha olefins (LAOs), which also may be referred to as terminal olefins or terminal alkenes, may be synthesized by several processes starting from low molecular weight feedstock materials. The two primary processes for synthesizing LAOs are oligomerization of ethylene and byproduct isolation from the Fischer-Tropsch synthesis. LAOs may also be isolated from a petroleum refinery stream. Depending on whether LAOs originate from petroleum or are produced synthetically, a variable extent of branching may be optionally present along the main carbon chain. In addition, variable amounts of terminal and/or non-terminal branched olefins may frequently be present in an olefinic feed comprising predominantly LAOs. The amount of branched olefins in a given olefinic feed may depend upon the carbon atom count of the LAOs that are present and the process by which the LAOs were produced.

[0004] Drilling operations within an earthen formation to promote extraction of a natural resource generally utilize a fluid to accomplish functions such as, for example, removing cuttings from the wellbore, lubricating and cooling the drill bit, supporting the drill pipe, maintaining stability of the hole, and providing hydrostatic pressure to prevent blowouts from occurring. Fluids used in conjunction with drilling or extending a wellbore may be referred to as “drilling muds” or “drilling fluids.”

[0005] LAOs may be incorporated in drilling fluids, either as a continuous phase or as a discontinuous phase. Thus, drilling fluids containing LAOs may be either oil-based (invert emulsion) or water-based (normal emulsion). Desirably, LAOs, particularly C_{16} and C_{18} LAOs, exhibit low toxicity toward aquatic organisms and undergo biodegradation, and they may further aid in conveying desired rheological properties to a drilling fluid. However, C_{16} and C_{18} LAOs exhibit relatively high pour point values, which may lead to problematic drilling fluid delivery for wellbores in certain locales. For example, when substantial LAOs are present in a drilling fluid, delivery to a subsea environment may be complicated by drilling fluid solidification resulting from exposure of the drilling fluid to cold subsea temperatures that may be encountered. Some commercial LAOs of relevance to the drilling industry have pour points of +7.2°C (C_{16}, freezing point = +3.9°C) and +18.3°C (C_{18}, freezing point = +17.8°C), where pour point is measured by ASTM D99 and freezing point is measured by ASTM D1015. The pour point of a 65:35 C_{16}/C_{18} LAO blend is about +13°C.

[0006] Linear internal olefins (LIOs) may overcome the pour point difficulties associated with corresponding LAOs having the same carbon atom count. Whereas LAOs feature a terminal double bond, LIOs instead include a double bond between two internal (interior) carbon atoms along the main carbon chain. LIOs may maintain the favorable environmental profile of LAOs. Compared to LAOs having the same carbon atom count, LIOs may exhibit lower pour point values and thereby maintain a liquid state at lower temperatures than is possible with the corresponding LAOs. The low pour points exhibited by LIOs may allow their delivery into wellbores located in environments that would otherwise be prohibitive due to drilling fluid solidification. Moreover, the environmental profile of LIOs may make these entities suitable for use in offshore drilling locales having stringent regulations for biodegradability and sediment toxicity, such as the Gulf of Mexico and off the coast of Brazil. Gulf of Mexico regulations for non-aqueous drilling fluids, for example, are specified by the U.S. Environmental Protection Agency in 77 FR No. 196, p. 61605. Sediment toxicity specifications therein are in accordance with ASTM E-1367. Anaerobic biodegradation specifications therein are in accordance with modified ISO 11734 275-D (275 day test), and corresponding aerobic biodegradation specifications are in accordance with OECD 306. Although LIOs may be particularly desirable for offshore drilling applications, they may also be suitable for drilling in onshore locales and in other applications as well.

[0007] Commercially sourced C_{16} and C_{18} LAOs usually contain about 75-90 weight percent ("wt%") LAOs, in conjunction with about 3-10 wt% internal olefins (IO) and about 5-15 wt% branched olefins (BO). LAOs having a lower carbon count may contain fewer branched olefins, and similarly, those having a higher carbon count may tend to contain more branched olefins. LAOs may be isomerized into LIOs using a variety of heterogeneous catalysts. However, depending on the catalyst, the conditions needed to affect isomerization may be rather harsh, and additional branching or cracking of the LAOs may occur under the isomerization reaction conditions. Cracking can result in undesirable product volume loss. The introduction of additional branching to the main carbon chain during isomerization can sometimes be undesirable due to the tendency for the branches, particularly C_{2+} branches and/or an excessive number of branches, to decrease olefin biodegradability. Extensive random branching can be especially problematic in this regard. Although a limited amount of branching in LIOs or in compositions comprising LIOs may be desirable for decreasing pour point, the present isomerization catalysts and methods do not introduce branches controllably or predictably.

[0008] Related publications include GB 1416317; US 2011/054192; US 3,928,485; US 3,405,196, and US 2,994,727.

SUMMARY

[0009] The present disclosure provides methods for synthesizing linear internal olefins (LIOs). The methods comprise providing an olefinic feed comprising one or more linear alpha olefins (LAOs), and interacting the olefinic feed with a catalyst composition comprising Na_2O on a solid support for a sufficient time to isomerize the one or more LAOs into one or more linear internal olefins (LIOs). The one or more LIOs are unbranched or contain no more branching than do the one or more LAOs of the olefinic feed.

[0010] The present disclosure also provides linear internal olefin (LIO) compositions comprising one or more LIOs. The LIO compositions comprise or consist essentially of one or more C_{14}-C_{20} LIOs that are unbranched, and about 5-15 wt% of one or more branched olefins. The LIO compositions have a pour point of about -6°C or less and are anaerobically biodegradable. Drilling fluids comprising the LIO compositions are also described.

[0011] The present disclosure also provides drilling methods comprising: providing a drilling fluid comprising a linear internal olefin (LIO) composition, and drilling a wellbore in the presence of the drilling fluid. The LIO composition comprises or consists essentially of one or more C_{14}-C_{20} LIOs and about 5-15 wt% of one or more branched olefins. The LIO composition has a pour point of about -6°C or less and is anaerobically biodegradable. Gulf of Mexico environmental, sediment toxicity, and biodegradation regulations may be met by the LIO compositions.

DETAILED DESCRIPTION

[0012] The present disclosure generally relates to olefin isomerization and, more specifically, to catalytic methods for isomerizing linear alpha olefins (LAOs) into linear internal olefins (LIOs) without inducing cracking or producing new branched olefins. LIO compositions and drilling methods employing LIOs produced via isomerization are also described herein.

[0013] As used herein, all weight percentages (wt%) are relative to the total amount of components in the composition referred to.

[0014] As discussed above, LAOs can be utilized in drilling fluids, but these compounds may be problematic in certain circumstances due to their relatively high pour points. For example, when delivering a drilling fluid containing substantial LAOs to a subsea wellbore, the cold subsea temperatures may undesirably solidify the drilling fluid. LIOs may be a suitable substitute for LAOs in drilling fluids in certain circumstances. LIOs may maintain the desirably low aquatic toxicity and favorable biodegradation profiles associated with LAOs. Advantageously, moving the double bond from the terminal position in LAOs to an internal position in LIOs affords a desirable decrease in pour point. However, LIOs are not straightforward to synthesize from small molecule feedstock materials. Moreover, many isomerization processes for converting LAOs into LIOs are prone to promoting substantial cracking or branching of the carbon chain in concert with isomerizing the position of the olefinic bond. Lower molecular weight olefins obtained from cracking may be unable to aid in conveying acceptable rheological properties to a drilling fluid and/or have unfavorable volatility. Olefins bearing excessive branching, on the other hand, may be undesirable for incorporation in drilling fluids due to their lower biodegradability.

[0015] The present disclosure demonstrates that LAOs may be isomerized into LIOs at high conversion rates and under mild conditions, such as at or near room temperature and atmospheric pressure, using a basic heterogeneous catalyst. Namely, the present disclosure demonstrates that a heterogeneous catalyst comprising sodium oxide (Na_2O) on a solid support, such as alumina (Al_2O_3), may convert LAOs into LIOs. Advantageously, the isomerization of LAOs into LIOs using Na_2O/Al_2O_3 takes place with essentially complete conversion of the LAOs into LIOs, such that no residual LAOs are detectable after a sufficient reaction time. Moreover, the isomerization of LAOs into LIOs takes place without the occurrence of substantial cracking or the formation of new branches on the carbon chain. In various embodiments, the LIOs and LIO compositions formed according to the present disclosure may exhibit no more branching than that present in the LAOs of the olefinic feed from which they were produced. That is, the heterogeneous catalysts of the present disclosure do not produce additional (new) branched olefins in the course of isomerizing LAOs into LIOs.

[0016] Accordingly, the present disclosure provides olefin compositions having low pour points and favorable toxicity and biodegradation profiles. In the case of the LIOs being predominantly C_{16}-C_{18} LIOs, for example, pour points lower than about -6°C may be obtained. In some cases, pour points as low as -17°C may be obtained, which may be due to a predominance of the cis isomer over the trans isomer in certain LIO compositions and/or due to location of the double bond further to the interior of the carbon chain, without being bound by theory or mechanism in either case. Incorporation of a limited amount of branched olefins in the olefin compositions (from the olefinic feed) may also favorably decrease the pour point while preserving biodegradability. The low pour points of LIOs may facilitate the formulation and use of drilling fluids in which the low pour points are maintained, along with favorable sediment toxicity and biodegradation profiles. It is to be appreciated that the methods disclosed herein may also be applicable to isomerizing LAOs of any desired carbon chain length, such as within a C_{10}-C_{30} range, for example. LIOs having carbon chain lengths above or below the C_{16}-C_{18} or C_{14}-C_{20} range may find utility in various applications and provide particular advantages therein that are distinct from those afforded during drilling applications. Moreover, depending upon the range of carbon chain lengths (olefin carbon count range) that is present, variable amounts of branched olefins from the olefinic feed may be present, as discussed in further detail below.

[0017] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" with respect to the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0018] Unless otherwise indicated, room temperature is about 21°C.

[0019] As used in the present disclosure and claims, the singular forms "a," "an," and "the" include plural forms unless the context clearly dictates otherwise.

[0020] The term "and/or" as used in a phrase such as "A and/or B" herein is intended to include "A and B," "A or B," "A", and "B."

[0021] For the purposes of the present disclosure, the numbering scheme for Groups of the Periodic Table disclosed in HAWLEY'S CONDENSED CHEMICAL DICTIONARY (13th ed., Wiley 1997) is used.

[0022] The term "hydrocarbon" refers to a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different numbers of carbon atoms. The term "C_n" refers to hydrocarbon(s) or a hydrocarbyl group having n carbon atom(s) per molecule or group, wherein n is a positive integer. Such hydrocarbon compounds may be one or more of linear, branched, cyclic, acyclic, saturated, unsaturated, aliphatic, or aromatic. When referenced with respect to an LAO or LIO, the term "C_n" refers to a hydrocarbyl group bearing at least one double bond.

[0023] The terms “hydrocarbyl” and “hydrocarbyl group” are used interchangeably herein. The term “hydrocarbyl group” refers to any C_1-C_{100} hydrocarbon group bearing at least one unfilled valence position when removed from a parent compound. “Hydrocarbyl groups” may be optionally substituted, in which the term “optionally substituted” refers to replacement of at least one hydrogen atom or at least one carbon atom with a heteroatom or heteroatom functional group. Heteroatoms may include, but are not limited to, B, O, N, S, P, F, Cl, Br, I, Si, Pb, Ge, Sn, As, Sb, Se, and Te. Heteroatom functional groups that may be present in substituted hydrocarbyl groups include, but are not limited to, functional groups such as O, S, S=O, $S(=O)_2$, NO_2, F, Cl, Br, I, NR_2, OR, SeR, TeR, PR_2, AsR_2, SbR_2, SR, BR_2, SiR_3, GeR_3, SnR_3, PbR_3, where R is a hydrocarbyl group or H. Suitable hydrocarbyl groups may include alkyl, alkenyl, alkynyl, aryl, heteroaryl, cycloalkyl, heterocyclyl, and the like, any of which may be optionally-substituted.

[0024] The term “alkyl” refers to a hydrocarbyl group having no unsaturated carbon-carbon bonds, and which may be optionally substituted.

[0025] The term “alkenyl” refers to a hydrocarbyl group having a carbon-carbon double bond, and which may be optionally substituted. The terms “alkene” and “olefin” are used synonymously herein. Similarly, the terms “alkenic” and “olefinic” are used synonymously herein. Unless otherwise noted, all possible geometric isomers are encompassed by these terms.

[0026] The terms “aromatic” and “aromatic hydrocarbon” refer to a hydrocarbon or hydrocarbyl group having a cyclic arrangement of conjugated pi-electrons that satisfy the Hückel rule. The term “aryl” is equivalent to the term “aromatic” as defined herein. The term “aryl” refers to both aromatic compounds and heteroaromatic compounds, either of which may be optionally substituted. Both mononuclear and polynuclear aromatic compounds are encompassed by these terms.

[0027] The terms “linear” and “linear hydrocarbon” refer to a hydrocarbon or hydrocarbyl group having a continuous carbon chain without side chain branching, in which the continuous carbon chain may be optionally substituted with heteroatoms or heteroatom groups.

[0028] The term “linear alpha olefin (LAO)” refers to an alkenic hydrocarbon bearing a carbon-carbon double bond at a terminal (end) carbon atom of the main carbon chain.

[0029] The term “linear internal olefin (LIO)” refers to an alkenic hydrocarbon bearing a carbon-carbon double bond at any carbon atom of the main carbon chain except for a terminal (end) carbon atom.

[0030] The terms "branch," "branched" and "branched hydrocarbon" refer to a hydrocarbon or hydrocarbyl group having a linear main carbon chain in which a hydrocarbyl side chain extends from the linear main carbon chain. Optional heteroatom substitution may be present in the linear main carbon chain or in the hydrocarbyl side chain. The term "unbranched" refers to a straight-chain hydrocarbon or hydrocarbyl group.

[0031] As used herein, the terms "well" and "wellbore" are used interchangeably and can include, without limitation, an oil, gas, or water production well, an injection well, or a geothermal well. As used herein, a "well" also includes at least one wellbore. A wellbore can include vertical, inclined, and/or horizontal portions, and it can be straight, curved, or bifurcated. As used herein, the term "wellbore" includes any cased portion, or any uncased, open-hole portion of the wellbore. A near-wellbore region is the subterranean material and rock of the subterranean formation surrounding the wellbore. As used herein, a "well" also includes the near-wellbore region. The near-wellbore region is generally considered to be the region within about 10 feet of the wellbore, although other distances both shorter and longer are also contemplated. As used herein, the phrases "into a well" and "into a wellbore" mean and include into any portion of the well, including into the wellbore or into the near-wellbore region via the wellbore.

[0032] A portion of a wellbore may be an open-hole or cased-hole. In an open-hole wellbore portion, a tubing or drill string may be placed into the wellbore. The tubing or drill string allows fluids to be circulated in the wellbore. In a cased-hole wellbore portion, a casing is placed and cemented into the wellbore, which can also contain a tubing or drill string. The space between two cylindrical shapes is called an annulus. Examples of an annulus include, but are not limited to: the space between the wellbore and the outside of a tubing or drill string in an open-hole wellbore; the space between the wellbore and the outside of a casing in a cased-hole wellbore; and the space between the inside of a casing and the outside of a tubing or drill string in a cased-hole wellbore. A drilling fluid may be circulated in the annulus, particularly for removing a portion of the drilling fluid from the wellbore.

[0033] In any embodiment of the present disclosure, catalyst compositions suitable for isomerizing LAOs into LIOs may be heterogeneous catalysts comprising sodium oxide (Na_2O) on a solid support, such as alumina (Al_2O_3). Other suitable solid supports may include, for example, silica or polymeric supports. According to more specific embodiments, suitable catalyst compositions comprising Na_2O on alumina may have a particle size ranging between about 10 microns and about 200 microns, or between about 80 microns and about 200 microns, or between about 20 microns and about 100 microns, or between about 40 microns and about

75 microns. In some or other embodiments, suitable catalyst compositions may have an average particle size ranging between about 80 microns and about 200 microns, including average particle sizes of about 100 microns or about 80 microns. In some or other embodiments, suitable catalyst compositions may comprise about 11-15 wt% sodium and have a particle density of approximately 3.14 g/cm^3 and a bulk density of approximately 0.884 g/cm^3.

[0034] In any embodiment, catalyst compositions suitable for practicing the present disclosure may have a surface area ranging from about 1 m^2/g to about 1000 m^2/g, or about 5 m^2/g to about 900 m^2/g, or about 50 m^2/g to about 500 m^2/g, or about 100 m^2/g to about 400 m^2/g. In some or other embodiments, suitable catalyst compositions may have a pore volume ranging between about 0.01 cm^3/g to about 10 cm^3/g, or about 0.1 cm^3/g to about 5 cm^3/g, or about 0.5 cm^3/g to about 3 cm^3/g, or about 1 cm^3/g to about 2.5 cm^3/g. In some or other embodiments, the catalyst compositions may contain a ratio of $Na_2O:Al_2O_3$ ranging from about 1:10,000 to about 10,000:1, or about 1:1,000 to about 1,000:1, or about 1:500 to about 500:1, or about 1:250 to about 250:1, or about 1:100 to about 100:1.

[0035] Other catalyst compositions that may be suitable for isomerizing LAOs into LIOs according to the disclosure herein may include, for example, sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) or sodium or potassium acetate ($NaO(O=C)CH_3$ or $KO(O=C)CH_3$) on a suitable solid support. In more specific embodiments, suitable catalyst compositions may include sodium carbonate, potassium carbonate, sodium acetate, potassium acetate, or any combination thereof disposed upon a solid support, such as aluminum oxide, silica or a polymer.

[0036] Accordingly, in any embodiment methods for isomerizing one or more LAOs may comprise: providing an olefinic feed comprising one or more LAOs, and interacting the olefinic feed with a catalyst composition comprising Na_2O on a solid support, such as alumina, for a sufficient time to isomerize the one or more LAOs into one or more LIOs. In more specific embodiments, the one or more LIOs are unbranched or contain no more branching than do the one or more LAOs from which they are formed. That is, the isomerization methods of the present disclosure do not introduce additional branches in the LIOs over those already present in the branched olefins within the olefinic feed. Thus, LIO compositions having no branching or a controlled amount of branching may be formed based upon the amount of branching present initially in the olefinic feed. In some or other specific embodiments, substantially no cracking takes place in conjunction with isomerizing the one or more LAOs into the one or more LIOs.

[0037] In any embodiment, the olefinic feed may comprise a liquid phase that is interacted with the catalyst composition. In more particular embodiments, the olefinic feed may be interacted neat with the catalyst composition. As used herein, the term "neat" refers to a liquid phase lacking solvent. Thus, according to some embodiments of the present disclosure, olefinic feeds may be interacted with the catalyst composition in the absence of solvent, wherein the olefinic feed is a liquid at the isomerization reaction temperature. The olefinic feed may be a liquid or a melted solid at the isomerization reaction temperature. It is to be appreciated that in alternative embodiments, however, the olefinic feed may be admixed with a suitable solvent in order to accomplish a similar result.

[0038] In any embodiment the reactor configurations suitable for interacting the catalyst composition with the olefinic feed may include a fluidized bed, a slurry bed, a trickle bed, or like reactor configuration for the catalyst composition. Fluidized bed reactor configurations for the catalyst composition may be particularly desirable, since removal of spent catalyst composition and introduction of additional (fresh) catalyst composition may be easily accomplished.

[0039] In any embodiment isomerization of the one or more LAOs into the one or more LIOs takes place at a temperature ranging between about 20°C and about 100°C. In more particular embodiments, isomerization takes place at a temperature ranging between about 20°C and about 60°C, or between about 20°C and about 50°C, or between about 20°C and about 40°C, or between about 20°C and about 30°C. In still more specific embodiments, isomerization takes place at about room temperature or between room temperature and about 40°C. In any embodiment, the isomerization reaction may be conducted initially at room temperature, and the temperature may rise during the reaction due to the exothermal nature of the isomerization process. In some or other embodiments, isomerization takes place at a temperature at which the one or more LAOs are in a liquid phase or state.

[0040] In any embodiment isomerization of the one or more LAOs into the one or more LIOs takes place at atmospheric pressure. Isomerization reaction conditions that are above atmospheric pressure are also possible in alternative embodiments of the present disclosure.

[0041] In any embodiment isomerization of the one or more LAOs into the one or more LIOs takes place under an inert atmosphere. Inert atmospheres may be favorable for maintaining activity of the catalyst composition. Suitable inert atmospheres may include, for example, helium, argon, neon, or nitrogen, for example. In some or other embodiments, isomerization of the one or more LAOs into the one or more LIOs takes place with substantial exclusion of water, such as through treatment of an LAO feed stream using a dryer bed employing a suitable desiccant.

[0042] In any embodiment isomerization of the one or more LAOs into the one or more LIOs takes place in air. Even in air (including exposure to water vapor in the air), at least some catalytic activity may be preserved.

[0043] In any embodiment the olefinic feed comprising the one or more LAOs may be purified before being contacted with the catalyst composition. Purification may remove water, stabilizers, oxygenates, or any combination thereof, which may aid in prolonging catalyst lifetime. According to certain embodiments, the olefinic feed may be contacted with activated alumina and zeolites to aid in suitably purifying the olefinic feed prior to isomerization. Other catalyst poisons may be similarly removed or partially removed during purification of the olefinic feed.

[0044] In any embodiment isomerization of the one or more LAOs into the one or more LIOs takes place over a period of time ranging between about 5 minutes and about 24 hours. In more specific embodiments, isomerization takes place over a period of time ranging between about 20 minutes and about 6 hours, or between about 30 minutes and about 4 hours, or between about 30 minutes and about 2 hours, or between about 10 minutes and about 90 minutes, or between about 10 minutes and about 30 minutes, or between about 20 minutes and about 90 minutes, or between about 20 minutes and about 60 minutes. In still more specific embodiments, isomerization takes place for about 1 hour or about 2 hours at about room temperature, during which time substantially all of the LAOs may be converted into LIOs. Other isomerization reaction times and isomerization temperatures may be selected such that substantially all of the LAOs undergo conversion into LIOs. Conversion of LAOs into LIOs may be considered to be substantially complete when less than about residual 5% LAOs or other alpha olefins are present. Less than about 1% LAOs or other alpha olefins may be present in any embodiment.

[0045] The catalyst composition may be present in various amounts with respect to the one or more LAOs. In any embodiment the catalyst composition may be present in an amount ranging between about 0.1% to about 50% by weight of the one or more LAOs. In more specific embodiments, the catalyst composition may be present in an amount ranging between about 0.05% to about 15% by weight of the one or more LAOs, or about 0.5% to about 25% by weight of the one or more LAOs, or between about 1% to about 15% by weight of the one or more LAOs, or between about 2% to about 12% by weight of the one or more LAOs. The referenced amounts of the catalyst composition represent the amount combined with the olefinic feed at the start of the isomerization reaction. Additional amounts of the catalyst composition may be added as the isomerization reaction progresses to replace spent catalyst and to maintain a desired isomerization reaction rate. The additional amounts of the catalyst composition may be added, neat or diluted, continuously or portion wise to the olefinic feed as the isomerization reaction occurs.

[0046] In illustrative embodiments, any LAO may be present in the olefinic feed. In more specific embodiments, the one or more LAOs may comprise a C_{10}-C_{30} grouping along the main carbon chain (*i.e.*, C_{10}-C_{30} LAOs). Illustrative LAOs that may be employed in the disclosure herein include, for example, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, and any variant thereof. As mentioned previously, isomerization of LAOs to form the corresponding LIOs takes place without introducing additional branching onto the carbon chain.

[0047] The olefinic feed may comprise any single LAO or any mixture comprising multiple LAOs, including two or more of the foregoing LAOs. C_{16}-C_{18} LAOs or C_{14}-C_{20} LAOs, in particular, may be desirable for formulation into drilling fluids, as discussed further herein. In more particular embodiments, the one or more LAOs may comprise or consist essentially of C_{14}-C_{20} LAOs, C_{16}-C_{18} LAOs, C_{16}/C_{18} LAOs, a C_{16} LAO, a C_{18} LAO, or any combination thereof.

[0048] In any embodiment, olefinic feeds suitable for use in the disclosure herein may further comprise about 5-30 wt% branched olefins and about 3-6 wt% internal olefins. In any embodiment, suitable olefinic feeds may comprise or consist essentially of C_{14}-C_{20} LAOs, about 5-15 wt% branched olefins, and about 3-6 wt% internal olefins. In still more specific embodiments, suitable olefinic feeds may comprise or consist essentially of C_{16} LAOs or a mixture of C_{16} and C_{18} LAOs, about 5-15 wt% branched olefins and about 3-6 wt% internal olefins. Other suitable olefinic feeds may comprise or consist essentially of C_{10} LAOs or a mixture of C_{10}-C_{14} LAOs and about 5-7 wt% branched olefins. In still other embodiments, suitable olefinic feeds may comprise or consist essentially of C_{30} LAOs or a mixture of C_{26}-C_{30} LAOs and about 25-30 wt% branched olefins.

[0049] LIO compositions comprising or consisting essentially of one or more LIOs formed from the corresponding LAOs may be made according to the disclosure herein. According to more specific embodiments, the LIO compositions may comprise one or more C_{14}-C_{20} LIOs that are unbranched, and about 5-15 wt% of one or more branched olefins. Such LIO compositions may have a pour point of -6°C or less and be anaerobically biodegradable (ISO 11734 275-D). In more specific embodiments of the present disclosure, the LIO compositions may comprise 90 wt% or more of the one or more LIOs. In some or other more specific embodiments, the LIO compositions may comprise or consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs. LIO compositions formed from olefinic feeds having a higher percentage of branched olefins may display a corresponding amount of branching in the LIO compositions, but new branches are not formed according to the methods described herein.

[0050] Any of the LIO compositions disclosed herein may be formulated into a drilling fluid and utilized in drilling methods, in any embodiment of the disclosure herein. In more particular embodiments, suitable drilling fluids and drilling methods may feature LIO compositions that comprise or consist essentially of one or more C_{14}-C_{20} LIOs that are unbranched, and about 5-15 wt% of one or more branched olefins. In more particular embodiments, the C_{14}-C_{20} LIOs may comprise or consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs. Other LIO compositions having different LIOs may be used in other applications, such as in paper sizing, for example.

[0051] Drilling methods of the present disclosure may feature one or more LIOs, such as the various LIO compositions described hereinabove. More specifically, in various embodiments, drilling methods of the present disclosure may comprise providing a drilling fluid comprising a LIO composition, and drilling a wellbore in the presence of the drilling fluid. The LIO composition may comprise or consist essentially of one or more C_{14}-C_{20} LIOs that are unbranched, and about 5-15 wt% of one or more branched olefins. The LIO composition has a pour point of -6°C or less and is anaerobically biodegradable (ISO 11734 275-D). According to more specific embodiments, the drilling fluids may meet environmental regulations for the Gulf of Mexico or coastal Brazil, for example. In some or other more specific embodiments, the C_{14}-C_{20} LIOs may comprise or consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs. In some or other embodiments, the LIO compositions within the drilling fluids may consist essentially of the one or more C_{14}-C_{20} LIOs and the one or more branched olefins. In such drilling fluids, C_{16}/C_{18} LIOs may constitute the majority of the LIO composition.

[0052] According to some embodiments, drilling fluids of the present disclosure may comprise at least one oil-based mud. In other embodiments, drilling fluids of the present disclosure may comprise at least one water-based mud. It is to be recognized that the term “oil-based” or “water-based” refers to the predominant continuous phase in the drilling fluid. Specifically, an oil-based mud contains a hydrocarbon or “oil” continuous (external) phase, and a water-based mud contains an aqueous or “water” continuous (external) phase. Inversion of either type of emulsion takes place during the course of a drilling operation. The LIO compositions disclosed herein may be present in either oil-based or water-based drilling fluid, optionally in further combination with other base oil components, including those described hereinafter.

[0053] Oil-based muds may include a base oil and one or more base oil additives. Numerous base oils are known in the art. Particular base oils that may be useful in the present disclosure include natural oils and synthetic oils, as well as unconventional oils (or mixtures thereof), which can be used unrefined, refined, or re-refined (the latter being known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one base oil property. Suitable purification processes may include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Re-refined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0054] The LIO compositions of the present disclosure may be used in combination with any of the base oils disclosed herein, or as an alternative to any of the base oils disclosed herein.

[0055] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted. Group II and/or Group III hydroprocessed or hydrocracked base stocks, including synthetic oils, are also well known base oils.

[0056] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (*e.g.*, polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alpha-olefin copolymers, for example). PAO base stocks are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8 to C_{14} olefins (*e.g.*, C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof) may be utilized as a base oil.

[0057] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, such as catalytically, or synthesized to provide high performance characteristics. Non-conventional or unconventional base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and/or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0058] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of base oil viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials, such as, for example, by distillation and subsequently subjected to a final wax processing step, which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; and (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (*i.e.*, hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates), such as hydrodewaxed or hydroisomerized/followed by catalytic and/or solvent dewaxing, dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by catalytic or solvent dewaxing, dewaxed F-T waxes, or mixtures thereof.

[0059] GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (*i.e.*, cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, may be essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low SAP products.

[0060] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0061] Some base oils may have an ester content of about 50 wt% or less, about 40 wt% or less, about 30 wt% or less, about 5 wt% or less, or about 1 wt% or less. Additionally or alternatively, some base oils may have an ester content of about 40 wt% or greater, or about 50 wt% or greater, about 70 wt% or greater, or about 90 wt% or greater.

[0062] Some base oils may have an aromatic content ranging from about 0.005 wt% to about 15 wt%, about 0.01 wt% to about 10 wt%, about 0.05 wt% to about 5 wt%, or about 0.1 wt% to about 1 wt%.

[0063] Water-based muds may include an aqueous carrier fluid, such as fresh water, salt water, sea water, or brine, optionally containing a water-miscible organic co-solvent such as an alcohol or glycol. As used herein, the term "brine" refers to a saturated aqueous salt solution. Brines may increase the weight of a drilling fluid, which can be advantageous for maintaining hydrostatic pressure in a wellbore. Illustrative weights may include a range of about 5 pounds per gallon (ppg) to about 20 ppg, or about 10 ppg to about 16 ppg. Suitable brines may include, for example, sodium chloride brines, sodium bromide brines, potassium chloride brines, potassium bromide brines, magnesium chloride brines, calcium chloride brines, and calcium bromide brines. Oil or similar hydrocarbons, including LIOs, can also be emulsified in the aqueous carrier fluid, according to some embodiments. In other embodiments, aqueous carrier fluids and water-based muds formed therefrom may be free or essentially free from oil or oil components. Suitable emulsifying agents and/or surfactants may be present, in any embodiment.

[0064] In addition to an oil-based mud or a water-based mud, drilling fluids of the present disclosure may also include further additives. The further additives may form a heterogeneous blend with a base oil or an aqueous carrier fluid. For either oil-based or water-based drilling fluids, the further additives may be dispersed in either the external phase or the internal phase of the drilling fluid. Additional additives that may be present include, but are not limited to, an acid, a base, a pH buffer, a viscosifier and/or a rheology modifier, an emulsifier, a wetting agent, a weighting agent, a fluid loss additive, a friction reducer, or any combination thereof.

[0065] Illustrative pH buffers and bases may be selected from the group consisting of magnesium oxide, potassium hydroxide, calcium oxide, and calcium hydroxide, for example. Lime is a commercially available example. The pH buffer or base can be present in a concentration in the range of about 0.5 to about 10.0 pounds per barrel (ppb) of the drilling fluid. The pH may range from a low of about 7, 8, 9, 10, 11, or 12 to a high of about 14, such as from 10 to 14.

[0066] Suitable viscosifiers and rheology modifiers may be selected from the group consisting of inorganic viscosifiers, fatty acids, including but not limited to dimer and trimer polycarboxylic fatty acids, diamines, polyamines, organophilic clays and combinations thereof. Commercially available examples of suitable viscosifiers include, but are not limited to, VG-PLUS™, available from M-I SWACO; and RHEMOD L™, TAU-MOD™, RM-63™, and combinations thereof, marketed by Halliburton Energy Services, Inc. According to some embodiments, the viscosifier and/or rheology modifier may be present in a concentration of at least 0.5 ppb of the drilling fluid. In more specific embodiments, the viscosifier and/or rheology modifier can also be present in a concentration of about 0.5 ppb to about 20 ppb, or a range of about 0.5 ppb to about 10 ppb, of the drilling fluid.

[0067] The drilling fluids may further include a solid lubricant, such as graphite, or a liquid friction reducer.

[0068] The drilling fluids can further include an emulsifier or a wetting agent. The emulsifier or wetting agent can be selected from the group consisting of tall oil-based fatty acid derivatives such as amides, amines, amidoamines, and imidazolines made by reactions of fatty acids and various ethanolamine compounds, vegetable oil-based derivatives, and combinations thereof. Commercially available examples of suitable emulsifiers include, but are not limited to, EZ MUL™ NT, INVERMUL™ NT, LE SUPERMUL™, and combinations thereof, marketed by Halliburton Energy Services, Inc., and MEGAMUL™, VERSAMUL™, VERSACOAT™, marketed by MI-SWACO. Commercially available examples of suitable wetting agents include, but are not limited to, DRILLTREAT™, OMC™, marketed by Halliburton Energy Services, Inc., and VERSAWET™, marketed by MI-SWACO. According to some embodiments, the emulsifier or wetting agent may be present in at least a sufficient concentration such that the drilling fluids maintain a stable emulsion or an invert emulsion. According to more specific embodiments, the emulsifier or wetting agent may be present in a concentration of at least 1 ppb of the drilling fluid. The emulsifier or wetting agent can also be present in a concentration in the range of about 1 to about 20 ppb of the drilling fluid.

[0069] The drilling fluids can further include a weighting agent. In any embodiment, the weighting agent can be selected from the group consisting of barite, hematite, manganese tetroxide, calcium carbonate, and combinations thereof. Commercially available examples of suitable weighting agents include, but are not limited to, BAROID™, BARACARB™, BARODENSE™, and combinations thereof, marketed by Halliburton Energy Services, Inc. and MICROMAX™, marketed by Elkem. According to some embodiments, the weighting agent may be present in a concentration of at least 10 ppb of the drilling fluid. The weighting agent can also be present in a concentration in the range of about 10 to about 1000 ppb, such as 10-800 ppb, of the drilling fluid.

[0070] The drilling fluids can further include a fluid loss additive. In any embodiment, the fluid loss additive can be selected from the group consisting of oleophilic polymers, including crosslinked oleophilic polymers and particulates. Commercially available examples of suitable fluid loss additives include, but are not limited to, VERSATROL™, available from M-I SWACO; and N-DRIL™ HT PLUS and ADAPTA™, marketed by Halliburton Energy Services, Inc. The fluid loss additive can also be present in a concentration in the range of about 0.5 to about 10 ppb of the drilling fluid.

[0071] The drilling fluids can further include an ester additive. The ester additive can be present in a concentration in the range of about 1 wt% to 20 wt%.

[0072] The drilling fluids may also optionally include one or more metal salts, MX'_y, where M is a Group 1 or Group 2 metal, X' is a halogen, and y is 1 to 2. Exemplary metal salts include, $NaCl$, KCl, $CaCl_2$, $MgCl_2$, and the like. The total amount of such salts in the drilling fluids may range between about 10 wt% to about 35 wt% in the water phase.

[0073] Water may also be present in oil-based drilling fluids at any convenient concentration, typically at a relatively low concentration, such as about 0.5 to about 20 wt%, about 0.5 to about 15 wt%, about 0.5 to about 12.5 wt%, about 0.5 to about 10 wt%, about 0.5 to about 7.5 wt%, about 0.5 to about 5 wt%, about 0.5 to about 2.5 wt%, about 0.5 to about 1 wt%, about 1 to about 10 wt%, about 1 to about 7.5 wt%, about 1 to about 5 wt%, about 1 to about 2.5 wt%, about 2.5 to about 10 wt%, about 2.5 to about 7.5 wt%, about 2.5 to about 5 wt%, about 5 to about 10 wt%, or about 5 to about 7.5 wt%.

[0074] The operation of drilling a wellbore in the presence of a drilling fluid may include creating a wellbore *de novo* or extending an existing wellbore. In any embodiment, a first drilling fluid may be used for drilling a first portion of the wellbore and a second drilling fluid may be used for drilling a second portion of the wellbore. For example, different drilling fluids may be used as the wellbore is extended and the subterranean conditions change. The drilling fluids of the present disclosure containing one or more LIOs may be used at any point of a drilling operation. In other embodiments, a single drilling fluid may be used for drilling both the first and second portions of a wellbore.

[0075] According to more specific embodiments of the present disclosure, a wellbore may be located in a subsea or similar underwater environment. Thus, in various embodiments of the present disclosure, drilling fluids comprising one or more LIOs may be used to create or extend a wellbore in a subsea or similar underwater environment.

[0076] Drilling operations may include any number of additional optional steps. In any embodiment, drilling operations may further include a step of removing at least a portion of the drilling fluid from the wellbore after introduction thereof. Drill cuttings (spoils) may also be removed from the wellbore in this process. Some drilling operations may include one or more of the following optional steps: mounting and cementing of well pipes; mounting a blowout preventer or lubricator in the top of the well; drilling, at a distance from a first well, a second well against a section of the first well to the effect that the second well achieves operational contact with the first well; mounting and cementing of well pipes in the second well; mounting a blowout preventer or lubricator in the top of the second well; whereafter the drilling from one of the first or second well continues down into the reservoir and the other well which is not drilled to the reservoir is filled wholly or partially with a fluid and a drilling tool is placed in the other well and the other well is subsequently closed so that the other well can be accessed at a later point in time, and that the tool is left in the other well so that this tool can establish a connection to the one of the first or second wells into which the drilling continued. Drilling methods of the present disclosure may therefore further include one or more steps of advancing a downhole tool in the wellbore. Suitable wellbore tools are not considered to be particularly limited and will be familiar to one having ordinary skill in the art.

[0077] Still other possible steps in a drilling operation may include one or more of the following: calculating a desired path for a well of interest relative to a reference well; measuring a position of the well of interest relative to the reference well at a location along the wellbore; calculating an actual path of the well of interest based at least in part on the measured position of the well of interest relative to the at least one reference well; comparing the actual path of the at least one well of interest to the desired path of the well of interest; and adjusting a drilling system to modify the actual path of the well of interest based at least in part on a deviation between the actual path of the well of interest and the desired path of the well of interest.

[0078] Thus, disclosed herein in numbered and lettered paragraphs are:

[0079] A. Isomerization methods. The isomerization methods comprise: providing an olefinic feed comprising one or more linear alpha olefins (LAOs); and interacting the olefinic feed with a catalyst composition comprising Na_2O on a solid support for a sufficient time to isomerize the one or more LAOs into one or more linear internal olefins (LIOs); wherein the one or more LIOs are unbranched or contain no more branching than do the one or more LAOs.

[0080] B. LIO compositions. The LIO compositions comprise: one or more C_{14}-C_{20} LIOs, the one or more C_{14}-C_{20} LIOs being unbranched; and about 5-15 wt% of one or more branched olefins; wherein the LIO composition has a pour point of about -6°C or less and is anaerobially biodegradable.

[0081] C. Drilling fluids. The drilling fluids comprise an LIO composition comprising: one or more C_{14}-C_{20} LIOs, the one or more C_{14}-C_{20} LIOs being unbranched; and about 5-15 wt% of one or more branched olefins; wherein the LIO composition has a pour point of about -6°C or less and is anaerobically biodegradable.

[0082] D. Drilling methods. The drilling methods comprise: providing a drilling fluid comprising a linear internal olefin (LIO) composition, the LIO composition comprising one or more C_{14}-C_{20} LIOs that are unbranched and about 5-15 wt% of one or more branched olefins; wherein the LIO composition has a pour point of about -6°C or less and is anaerobically biodegradable; and drilling a wellbore in the presence of the drilling fluid.

[0083] Embodiments A-D may have one or more of the following additional elements in any combination:

[0084] Element 1: wherein the solid support comprises alumina.

[0085] Element 2: wherein the olefinic feed is interacted with the catalyst composition at room temperature.

[0086] Element 3: wherein the olefinic feed is interacted with the catalyst composition at a temperature ranging between room temperature and about 40°C.

[0087] Element 4: wherein the olefinic feed is interacted neat with the catalyst composition.

[0088] Element 5: wherein the olefinic feed is interacted with the catalyst composition in a fluidized bed.

[0089] Element 6: wherein the catalyst composition has a particle size ranging between about 40 microns and about 75 microns.

[0090] Element 7: wherein the olefinic feed comprises C_{10}-C_{30} LAOs.

[0091] Element 8: wherein the olefinic feed comprises a C_{16} LAO, a C_{18} LAO, or any combination thereof.

[0092] Element 9: wherein the olefinic feed comprises C_{14}-C_{20} LAOs.

[0093] Element 10: wherein the olefinic feed consists essentially of C_{14}-C_{20} LAOs, about 5-15 wt% branched olefins, and about 3-6 wt% internal olefins.

[0094] Element 11: wherein the olefinic feed consists essentially of C_{16} LAOs or a mixture of C_{16} and C_{18} LAOs, about 5-15 wt% branched olefins, and about 3-6 wt% internal olefins.

[0095] Element 12: wherein substantially no cracking or branching occurs upon isomerizing the one or more LAOs to form the one or more LIOs.

[0096] Element 13: wherein the LIO composition comprises 90 wt% or more of the one or more LIOs.

[0097] Element 14: wherein the one or more C_{14}-C_{20} LIOs comprise C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

[0098] Element 15: wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

[0099] Element 16: wherein the LIO composition consists essentially of the C_{14}-C_{20} LIOs and the one or more branched olefins.

[0100] Element 17: wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs.

[0101] Element 18: wherein the wellbore is located in a subsea environment.

[0102] Element 19: wherein the one or more LAOs are commercially produced.

[0103] To facilitate a better understanding of the embodiments described herein, the following examples of various representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the present disclosure.

EXAMPLES

[0104] All example experiments were performed in a glove box under N_2 to eliminate the effects of oxygen and moisture upon catalyst performance. The Na_2O on alumina catalyst was in powder form having an N_2 BET surface area of 80-130 m^2/g. The catalyst particles ranged from 40 to 75 microns in size. The catalyst contained 11-15 wt% sodium and had a particle density of 3.14 g/cm^3. Pour point values were measured using ASTM method D5950- "Standard Test Method for Pour Point of Petroleum Products (Automatic Tilt Method)."

[0105] Example 1: A sample of 10 g of 99.5 wt% C_{16} LAOs (Sigma-Aldrich) was weighed into a 30 mL scintillation vial and combined with 1 g of the Na_2O/Al_2O_3 catalyst (10 wt% catalyst loading with respect to olefinic feed). The catalyst was added to the C_{16} LAOs over a period of about 5 seconds. The reaction mixture was stirred as a slurry at 500 rpm at 21°C over 1 hour. After 1 hour, 1 mL of water was added to the reaction mixture to quench the catalyst.

[0106] After quenching, the reaction mixture was filtered from the catalyst and analyzed using nuclear magnetic resonance (^{1}H NMR). ^{1}H NMR was used to identify the ratio of LAOs, LIOs and branched olefins in the isomerized product. The analyses showed essentially complete (>95%) conversion of the C_{16} LAOs into the corresponding LIOs with no introduction of branching to the carbon chain. Less than 1 wt% of LAOs remained in the reaction product.

[0107] The pour point of the isomerized product was -15.2°C.

[0108] Example 2: A sample of 300 g of 92 wt% C_{16} LAOs containing about 6% branched C_{16} vinylidenes was weighed into a 500 mL roundbottom flask and combined with 5 g of the Na_2O/Al_2O_3 catalyst (1.67 wt% catalyst loading with respect to olefinic feed). The catalyst was added to the C_{16} LAOs over a period of about 5 minutes. The reaction mixture was stirred as a slurry at 500 rpm at 21°C over 1 hour. After 1 hour, 5 mL of water was added to the reaction mixture to quench the catalyst.

[0109] After quenching, the reaction mixture was filtered from the catalyst and analyzed using gas chromatography (GC). GC analyses were conducted by hydrogenating 1 g of the reaction product over an Ir catalyst and analyzing the paraffinic product. The GC analyses showed 0% trace olefins, 94% linear olefins (analyzed as the corresponding paraffins), and 6% branched olefins (analyzed as the corresponding paraffins), which is consistent with the amount of branching in the olefinic feed.

[0110] The pour point of the isomerized product was -5.5°C.

[0111] Example 3: A sample of 300 g of 92 wt% C_{16} LAOs containing about 6% branched C_{16} vinylidenes was weighed into a 500 mL roundbottom flask and combined with 10 g of the Na_2O/Al_2O_3 catalyst (3.33 wt% catalyst loading with respect to olefinic feed). The catalyst was added to the C_{16} LAOs over a period of about 5 minutes. The reaction mixture was stirred as a slurry at 500 rpm at 21°C over 1 hour. After 1 hour, 10 mL of water was added to the reaction mixture to quench the catalyst.

[0112] After quenching, the reaction mixture was filtered from the spent catalyst and analyzed using GC as described in Example 2. The analyses showed essentially complete conversion of the C_{16} LAOs into the corresponding LIOs without introducing additional branching to the carbon chain.

[0113] The pour point of the isomerized product was -9.5°C. The lower pour point of Example 3 compared to Example 2 is believed to be due to a greater cis/trans isomer ratio and/or additional internal shift of the olefinic bond when using a higher amount of catalyst.

[0114] Example 4: A sample of 300 g of C_{16}/C_{18} LAOs (65 wt% C_{16} LAOs of total LAOs, 35 wt% C_{18} LAOs of total LAOs, about 90 wt% LAOs total, with the remainder being 3-6 wt% internal olefins and 5-10 wt% branched olefins) was weighed into a 500 mL roundbottom flask and combined with 5 g of the Na_2O/Al_2O_3 catalyst (1.67 wt% catalyst loading with respect to olefinic feed). The catalyst was added to the C_{16}/C_{18} LAOs over a period of about 5 minutes. The reaction mixture was stirred as a slurry at 500 rpm at 40°C over 1 hour. After 1 hour, 5 mL of water was added to the reaction mixture to quench the catalyst.

[0115] After quenching, the reaction mixture was filtered from the spent catalyst and analyzed using GC as described in Example 2. The analyses showed essentially complete conversion of the C_{16}/C_{18} LAOs into the corresponding LIOs without introducing additional branching to the carbon chain.

[0116] The pour point of the isomerized product was -2.6°C.

[0117] Example 5: A sample of 300 g of C_{16}/C_{18} LAOs (65 wt% C_{16} LAOs of total LAOs, 35 wt% C_{18} LAOs of total LAOs, about 90 wt% LAOs total, with the remainder being 3-6 wt% internal olefins and 5-10 wt% branched olefins) was weighed into a 500 mL roundbottom flask and combined with 10 g of the Na_2O/Al_2O_3 catalyst (3.33 wt% catalyst loading with respect to olefinic feed). The catalyst was added to the C_{16}/C_{18} LAOs over a period of about 5 minutes. The reaction mixture was stirred as a slurry at 500 rpm at 40°C over 2 hours. After 2 hours, 10 mL of water was added to the reaction mixture to quench the catalyst.

[0118] After quenching, the reaction mixture was filtered from the catalyst and analyzed using GC as described in Example 2. The analyses showed essentially complete conversion of the C_{16}/C_{18} LAOs into the corresponding LIOs without introducing additional branching to the carbon chain.

[0119] The pour point of the isomerized product was -8.8°C.

[0120] All documents described herein are incorporated by reference herein for purposes of all jurisdictions where such practice is allowed, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the disclosure be limited thereby. For example, the compositions described herein may be free of any component, or composition not expressly recited or disclosed herein. Any method may lack any step not recited or disclosed herein. Likewise, the term "comprising" is considered synonymous with the term “including.” Whenever a method, composition, element or group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

CLAIMS

1. A method comprising:

providing an olefinic feed comprising one or more linear alpha olefins (LAOs); and

interacting the olefinic feed with a catalyst composition comprising Na_2O on a solid support for a sufficient time to isomerize the one or more LAOs into one or more linear internal olefins (LIOs),

wherein the one or more LIOs are unbranched or contain no more branching than do the one or more LAOs.

2. The method of claim 1, wherein the solid support comprises alumina.

3. The method of claim 1 or claim 2, wherein the olefinic feed is interacted with the catalyst composition at room temperature.

4. The method of claim 1 or claim 2, wherein the olefinic feed is interacted with the catalyst composition at a temperature ranging between room temperature and about 40°C.

5. The method of any one of claims 1-4, wherein the olefinic feed is interacted neat with the catalyst composition.

6. The method of any one of claims 1-5, wherein the olefinic feed is interacted with the catalyst composition in a fluidized bed.

7. The method of any one of claims 1-6, wherein the catalyst composition has a particle size ranging between about 40 microns and about 75 microns.

8. The method of any one of claims 1-7, wherein the olefinic feed comprises C_{10}-C_{30} LAOs.

9. The method of any one of claims 1-7, wherein the olefinic feed comprises a C_{16} LAO, a C_{18} LAO, or any combination thereof.

10. The method of any one of claims 1-7, wherein the olefinic feed comprises C_{14}-C_{20} LAOs.

11. The method of any one of claims 1-7, wherein the olefinic feed consists essentially of C_{14}-C_{20} LAOs, about 5-15 wt% branched olefins, and about 3-6 wt% internal olefins.

12. The method of any one of claims 1-7, wherein the olefinic feed consists essentially of C_{16} LAOs or a mixture of C_{16} and C_{18} LAOs, about 5-15 wt% branched olefins, and about 3-6 wt% internal olefins.

13. The method of any one of claims 1-12, wherein substantially no cracking or branching occurs upon isomerizing the one or more LAOs to form the one or more LIOs.

14. A linear internal olefin (LIO) composition comprising:

one or more C_{14}-C_{20} LIOs, the one or more C_{14}-C_{20} LIOs being unbranched; and about 5-15 wt% of one or more branched olefins,

wherein the LIO composition has a pour point of about -6°C or less and is anaerobically biodegradable.

15. The LIO composition of claim 14, wherein the LIO composition comprises 90 wt% or more of the one or more LIOs.

16. The LIO composition of claim 14 or claim 15, wherein the one or more C_{14}-C_{20} LIOs comprise C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

17. The LIO composition of claim 14 or claim 15, wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

18. The LIO composition of claim 14, wherein the LIO composition consists essentially of the C_{14}-C_{20} LIOs and the one or more branched olefins.

19. A drilling fluid comprising the LIO composition of claim 14.

20. The drilling fluid of claim 19, wherein the one or more C_{14}-C_{20} LIOs comprise C_{16} LIOs

or a mixture of C_{16} and C_{18} LIOs.

21. The drilling fluid of claim 19, wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

22. A drilling method comprising:

providing a drilling fluid comprising a linear internal olefin (LIO) composition, the LIO composition comprising one or more C_{14}-C_{20} LIOs that are unbranched and about 5-15 wt% of one or more branched olefins,

wherein the LIO composition has a pour point of about -6°C or less and is anaerobically biodegradable; and

drilling a wellbore in the presence of the drilling fluid.

23. The drilling method of claim 22, wherein the one or more C_{14}-C_{20} LIOs comprise C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

24. The drilling method of claim 22, wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs or a mixture of C_{16} and C_{18} LIOs.

25. The drilling method of claim 22, wherein the one or more C_{14}-C_{20} LIOs consist essentially of C_{16} LIOs.

26. The drilling method of claim 22, wherein the LIO composition consists essentially of the one or more C_{14}-C_{20} LIOs and the one or more branched olefins.

27. The drilling method of any one of claims 22-26, wherein the LIO composition comprises 90 wt% or more of the one or more LIOs.

28. The drilling method of any one of claims 22-27, wherein the wellbore is located in a subsea environment.

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-13, 28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/033316

A. CLASSIFICATION OF SUBJECT MATTER

C07C 2/10(2006.01)i, C07C 5/25(2006.01)i, B01J 23/04(2006.01)i, C09K 8/34(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 2/10; C07C 13/00; C07C 5/22; C07C 5/23; C07C 5/25; C09K 7/02; B01J 23/04; C09K 8/34

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 alpha olefin (LAO), linear internal olefin (LIO), Na2O, alumina, isomerization, drilling fluid, branched olefin

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SiGNa Isomerization Report FINAL, "Catalytic isomerization of α-olefin to internal olefin", 2013, pages 1-4 See pages 1-3.	1-4
A		14-27
X	US 5589442 A (GEE, JEFFREY C. et al.) 31 December 1996 See columns 1-4.	14-27
X	US 2009-0163757 A1 (GEE, JEFFERY C.) 25 June 2009 See paragraphs [0018]-[0020], [0055]-[0063].	14-18
A	US 2005-0070747 A1 (BROWN, DAVID STEPHEN et al.) 31 March 2005 See the whole document.	1-4,14-27
A	US 2006-0293549 A1 (SIGL, MARCUS et al.) 28 December 2006 See the whole document.	1-4,14-27

☐ 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 16 September 2019 (16.09.2019)	Date of mailing of the international search report **18 September 2019 (18.09.2019)**
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer KWON, YONGKYONG Telephone No. +82-42-481-3371

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/033316

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