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PROCESS FOR WELL FLUIDS BASE OIL VIA METATHESIS OF ALPHA-OLEFINS

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ABSTRACT

Disclosed is a process for preparation of compositions having utility as well fluid base oils. The process involves metathesis of alpha-olefins followed by isomerization of the metathesis products. The base oils resulting from the process of this invention are environmentally friendly in that they are only mildly toxic to marine life and have very low pour point temperatures. These properties make the base oils ideal candidates for use as components of well fluids for cold climates and offshore applications.

PROCESS FOR WELL FLUIDS BASE OIL VIA METATHESIS OF ALPHA-OLEFINS

RELATIONSHIP TO PRIOR APPLICATIONS

[0001] (Not Applicable)

STATEMENT REGARDING FEDERALLY FUNDED RESEARCH

[0002] (Not Applicable)

FIELD OF THE INVENTION

[0003] The invention relates generally to a process for making compositions having utility as base oils for well fluids. The multi-step process involves metathesis of alpha-olefins followed by isomerization of the metathesis products. The base oils resulting from the process of this invention are environmentally friendly and have very low pour point temperatures. These properties make the base oils ideal candidates for use as components of well fluids for cold land drilling climates and also for cold offshore drilling applications. The products formed by the metathesis portion of the process (absent the isomerization step) are also valuable and have utility (as produced) as components of lube oils, lube oil additives, alkenyl succinic anhydrides, surfactants, and plasticizers or as precursors to selected members of the preceding list.

BACKGROUND OF THE INVENTION

[0004] Historically, first crude oils, then diesel oils and, more recently, mineral oils have been used in formulating well fluids. Due to problems of toxicity and persistence which are associated with these oils, and which are of special concern for offshore use, the industry is developing well fluids that are based on "pseudo-oils". Examples of such oils are fatty acid esters and synthetic hydrocarbons such as poly(alpha)olefins. Fatty acid ester based oils have excellent environmental properties, but well fluids made with these esters tend to have lower densities and are prone to hydrolytic instability. Poly(alpha)olefin based well fluids can be formulated to high densities, have good hydrolytic stability and low toxicity. They are, however, somewhat less biodegradable than esters, they are expensive and the fully weighted, high density fluids tend to be overly viscous, especially when used in cold climates. A most recent trend in the industry is the use of base oils comprising predominantly linear internal olefins. The present invention offers a new and novel metathesis route to liquid internal olefins that have better toxicity properties than the liquid internal olefins currently used in well fluid base oils. Additionally, the internal olefins made by the process of this invention also have very low pour point temperatures sufficient for extreme cold and/or offshore drilling applications. There is a continuing need for improved well fluid base oils that are environmentally acceptable and have pour point temperatures in the range of about -15°C . to about -40°C . The present invention addresses this need via a process that includes a metathesis reaction followed by an isomerization of the product prepared by metathesis.

INVENTION SUMMARY AND REVIEW OF PRIOR ART

[0005] The present invention resides in a process for the preparation of compositions that are especially favorable for

use as well fluid base oils. The well fluid base oils prepared by the process of this invention are not only environmentally acceptable but also have especially advantageous and unexpectedly low pour point temperatures.

[0006] The base oil compositions of this invention are prepared by a process that involves at least one chemical reaction. For the purposes of this disclosure, alpha olefin is intended to mean a mono-olefin having the carbon-carbon double bond after the terminal (first) carbon atom. In the first (metathesis) reaction, an alpha-olefin feed is provided and then subjected to metathesis conditions. The linear alpha-olefin feed to the metathesis process is not 100 percent linear alpha-olefins. A more precise feed definition will be recited later. Other materials are typically present in the feed. A non-exhaustive listing of such other materials includes internal olefins, vinylidene olefins, tri-substituted olefins, and branched (non-linear) olefins. The linear alpha-olefin (or mixture of several linear alpha-olefins) feed is subjected to metathesis conditions in the presence of a metathesis catalyst. Linear alpha-olefins having an integer number of carbon atoms in the range of about 4 to about 22 are envisioned as suitable for the metathesis feed. In the metathesis step, the linear alpha-olefins react with one another to form linear internal olefins. If only one linear alpha-olefin having n carbon atoms (where n is an integer in the range of 4 to 22) is subjected to metathesis (known as self-metathesis), then the product formed will be a linear internal olefin having $(2n-2)$ carbon atoms with the double bond at the center position, i.e., after carbon atom n . If a mixture of several linear alpha-olefins is subjected to metathesis (known as cross-metathesis), then several linear internal olefin products are formed, all of which will have the double bond at an internal position. If the shortest alpha-olefin fed to metathesis has 4 carbons, then the internal olefins formed from metathesis will have the double bond at least after or even more internal than carbon atom No. 3.

[0007] The centralized double bond olefins of self metathesis and the internal olefins of cross metathesis are valuable chemical compositions and substances that have important commercial applications other than as a component of well fluid base oils. When used for preparation of well fluid base oils, the base oils are found to have lower toxicity than base oils comprised of currently used internal olefins. The pour point temperatures of well fluid base oils made from these metathesis liquids are useful in cold climates. In some applications, such as extremely cold land or offshore drilling, it is desirable to have even lower pour point temperatures than those exhibited by the metathesis liquids. Applicants have found that an unexpectedly large change in pour point temperature can be achieved by isomerizing the liquid products from the self and/or cross metathesis process. The isomerization is conducted under isomerization conditions and in the presence of a catalyst which is typically used for olefin isomerization, including both (1) migration of the double bond within the olefin molecule, and (2) skeletal rearrangement of the olefin molecule. Surprisingly, when used as well fluid base oils, the metathesized and isomerized liquids retain or improve their salient environmental characteristics and, in the process, produce well fluid base oils having pour point temperatures about 15°C . to 40°C . lower than those obtained absent the isomerization step.

[0008] U.S. Pat. No. 5,589,442 (Gee et al.) discloses well fluid base oil which is predominantly unbranched (linear)

internal olefins. The Gee et al. patent discloses the use of C_{12} to C_{24} olefins in their mixture, preferably C_{14} - C_{18} olefins. The disclosure of the Gee et al. patent permits the presence of some branched olefins in their mixtures (0-50 wt %) with the remainder being linear olefins. The disclosure of the Gee et al. patent also permits the presence of some alpha olefins in their mixture (0-20 wt %) with the remainder being internal olefins. The pour point temperature of the preferred embodiment of the Gee et al. disclosure is -5°C . with some formulations having pour point temperatures as low as -9°C . This application may be differentiated from the disclosure of U.S. Pat. No. 5,589,442 in that it is directed to production of well fluid base oil having pour point temperatures in the range of -15°C . to -30°C . with an especially preferred embodiment having a pour point temperature of -36°C . Also, the liquids produced by the process of this disclosure have improved toxicity properties over those disclosed in the Gee et al. reference.

[0009] U.S. Pat. Nos. 5,741,759, 6,057,272 (both also Gee et al.), 6,323,157 (Carpenter et al.), and the Gee et al. '442 patent referenced above all disclose the use of commercially available linear alpha olefin or linear alpha olefin mixtures in the range C_{14} to C_{18} as the starting material for their base oil according to the examples in these references. These are then transformed into internal olefins for use in well fluid base oils. Alpha olefins in this carbon count range are extremely valuable as compared to alpha olefins in the range of C_4 to C_{12} . Applicants' process discloses the use of these lower carbon chain alpha olefins as starting materials to produce internal olefin, for example, in the range C_{14} to C_{18} thus offering a substantial commercial advantage over the disclosure of the four references cited above.

[0010] APCT patent application published as patent document WO 01/46096 discloses a process for production of drilling fluid made from metathesis products of C_4 to C_{10} olefins. Applicants' disclosure may be distinguished from this reference as follows: (1) applicants metathesis is conducted in the presence of a heterogeneous catalyst system as opposed to the homogeneous system of this reference, (2) applicants use a rhenium metathesis catalyst system, and in a preferred embodiment, as opposed to the metathesis catalyst metals disclosed by this reference, and (3) applicants perform metathesis followed by isomerization whereas there is no isomerization step disclosed in WO 01/46096,

[0011] An article in "Chem. Eng. Prog.", 1979, V 75, No. 1, Pages 73-76 entitled SHELL'S HIGHER OLEFINS PROCESS (SHOP) by authors Freitas and Gum discloses a four-step process aimed at production of internal olefins in the range useful for detergents manufacture. The steps in the SHOP process are (1) ethylene oligomerization to produce an alpha-olefin, (2) purification of alpha-olefins to remove catalyst poisons, (3) isomerization of the alpha-olefin to produce internal olefin, and (4) disproportionation (aka metathesis) to form the desired chain length internal olefins. Applicants disclosure may be distinguished from this reference in a number of different ways including: (A) applicants' process is directed to metathesis first followed by isomerization instead of isomerization followed by disproportionation and (B) the source of the metathesized alpha-olefins forms no part, per se, of Applicants' disclosed process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] It should be noted that the term "comprising" is used frequently throughout the description of this invention and also in the appended claims. "Comprising", as used in this application and the appended claims is defined as "specifying the presence of stated features, integers, steps, or components as recited, but not precluding the presence or addition of one or more other steps, components, or groups thereof". Comprising is different from "consisting of", which does preclude the presence or addition of one or more other steps, components, or groups thereof.

[0013] For the purposes of this invention, a well fluid is intended to be any fluid or near fluid used in the rotary method of drilling wells, chiefly for gas and oil, and is not intended to be restricted only to so-called drilling muds. A non-limiting list of well fluids includes drilling muds, spotting fluids, lubricating additives, and other products for the treatment of subterranean wells. Also, for the purposes of this invention, internally isomerized olefins are defined to comprise olefins having only a single double bond (mono-olefin) joining adjacent carbon atoms other than the terminal (or alpha) carbon atom of the carbon chain. Mixtures of internal olefin isomers implies that several different double bond isomers are present, e.g., some of the olefins may have a double bond connecting carbon atom #8 to carbon atom #9, some double bonds may connect carbon atom #7 to carbon atom #8, etc. For each double bond isomer, generally, there will be at least two stereo isomers commonly referred to as the cis and trans forms. Mixtures of internal olefin isomers may also imply the presence of both linear (unbranched) and branched olefin isomers.

[0014] The present invention relates to a group of synthetic liquid hydrocarbons and to well fluids based on them, especially to well fluids which are useful in the rotary drilling process used for making wells into subterranean formations containing oil, gas or other minerals.

[0015] The rotary drilling process is used for making wells for the production of oil, gas and other subterranean minerals such as sulfur. In rotary drilling operations, a drill bit at the end of a drill string is used to penetrate the subterranean formations. This drill bit may be driven by a rotating drill string or a drill motor powered, for example, by hydraulic power. During the rotary drilling operation, a fluid, conventionally referred to as a drilling mud, is circulated from the drilling equipment on the surface down to the drill bit where it escapes around the drill bit and returns to the surface along the annular space between the drill bit and the surrounding subsurface formations. The drilling mud lubricates the down-hole equipment and serves as a carrier to bring the formation cuttings to the surface where they can be separated from the mud before it is recirculated. In addition, the drilling mud serves to counterbalance formation pressures and may also form a cake around the walls of the borehole to seal the formations.

[0016] The lubricating action of the drilling mud is particularly important with the conventional rotating drill string since it provides a lubricant or cushion between the rotating drill pipe and the walls of the borehole, helping to prevent sticking of the drill string in the hole. The characteristics and performance of drilling muds are described, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Third

Edition, John Wiley and Sons, 1982, under Petroleum (Drilling Muds). This reference discloses a description of drilling muds and the materials used in formulating them.

[0017] Drilling muds are usually classified as either water based muds or oil-based muds, depending upon the character of the continuous phase of the mud, although water-based muds may contain oil and oil-based muds may contain water. Water-based muds conventionally comprise a hydratable clay, usually of the montmorillonite family, suspended in water with aid of suitable surfactants, emulsifiers and other additives including salts, pH control agents and weighting agents such as barite. The water makes up the continuous phase of the mud and is usually present in any amount of at least 50 volume percent of the entire composition. Oil is also usually present in minor amounts but will typically not exceed the amount of the water so that the mud will retain its character as a water-continuous phase material. Oil-based muds generally use a hydrocarbon oil as the main liquid component with other materials such as clays or colloidal asphalts added to provide the desired viscosity together with emulsifiers, gellants and other additives including weighting agents. Water may be present in greater or lesser amounts but will usually not be greater than 50 volume percent of the entire composition. If more than about 10 weight percent water is present, the mud is often referred to as an invert emulsion, i.e. a water-in-oil emulsion. In invert emulsion fluids, the amount of water is typically up to about 40 weight percent with the oil and the additives making up the remainder of the fluid. Under appropriate conditions, the well fluid base oils of the present invention may comprise any of the above-described materials, i.e., water-based fluids, oil-based fluids, and invert emulsion fluids.

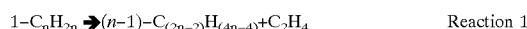
[0018] Historically, oil-based muds were conventionally formulated with diesel oil or kerosene as the main oil component as these hydrocarbon fractions generally possess the requisite viscosity characteristics. They do, however, possess the disadvantage of being relatively toxic to marine life and the discharge of drilling muds containing these oils into marine waters is usually strictly controlled because of the serious effects that the oil components may have on marine organisms. The control is particularly acute for marine life that are commercially important as food. For this reason, offshore drilling rigs must return oil-based muds to shore after they have been used whereas water-based muds may generally be discharged into the ocean without any deleterious effects.

[0019] Oil-based muds may be formulated to be environmentally acceptable by the use of oils that possess low inherent toxicity to marine organisms and good biodegradability. These properties are more generally found in hydrocarbons with low aromaticity. For these reasons, well fluids based on paraffins might be considered desirable. On the other hand, linear paraffins tend to have high pour point temperatures and the higher molecular weight fractions tend to be waxy so that in the low temperature environments frequently encountered in offshore drilling, there is a significant risk that waxy paraffin deposits will be formed in the down hole equipment or in the riser connecting the sea bed to the drilling equipment. In either event, this is unacceptable with the result that highly paraffinic oils have not achieved any significant utility as bases for well fluids.

[0020] The use of olefins as base oils for well fluids represents yet another way to avoid the toxicity associated with the use of aromatics in well fluid base oils and has become a pursued alternative in recent years. Linear alpha and internal olefins have all found application as components of well fluid base oils. The present invention is directed, in part, to a process for production of well fluid base oils comprising intermediate to long chain (predominantly unbranched) internal olefins. In this context, predominantly unbranched is intended to mean at least 50 weight percent.

[0021] The linear alpha-olefin feed that is subjected to self-metathesis or cross metathesis will generally include olefins in the range having from about 4 to about 22 carbon atoms. Preferably, the range will be from about 6 to about 20 carbon atoms, and most preferably from about 8 to about 18 carbon atoms. For this invention, the linear alpha-olefin feed is defined to be at least 90% (by weight) linear alpha-olefin for olefins in the range of about 4 to about 12 carbon atoms. The linear alpha-olefin feed is further defined to be at least 70% (by weight) linear alpha-olefin for olefins in the range of about 13 to about 20 carbon atoms. The linear alpha-olefin feed is defined to be at least 45% (by weight) linear alpha-olefin for olefins having more than 20 carbon atoms. A non-exhaustive list of other materials which may be present in the linear alpha-olefin feed include internal olefins (branched or linear), vinylidene olefins, tri-substituted olefins, and branched (non-linear) alpha-olefins. The self or cross metathesis transforms the linear alpha-olefin feed into predominantly linear internal olefins. For the purpose of this invention, a linear deep internal olefin is defined to be a linear olefin that has its double bond in the range of after carbon atom 3 or further toward the center of the molecule. According to this definition (at least for this invention) there will be no deep internal olefins having fewer than 6 carbon atoms.

[0022] Reaction 1, as given below, shows a self-metathesis reaction, for the desired or main reaction, in generic form.



[0023] In Reaction 1, the substance $1-C_nH_{2n}$ is a normal (unbranched) 1 olefin (alpha-olefin), n is an integer and has a value in the range of about 4 to about 22, C_2H_4 is ethylene, and $(n-1)-C_{(2n-2)}H_{(4n-4)}$ is a linear (unbranched) internal olefin with the double bond after carbon atom $(n-1)$, i.e., the double bond is directly in the middle of the compound. In actuality, it would require two moles of reactant to produce a mole of ethylene and a mole of desired metathesis product as shown in Reaction 1. For the sake of simplicity, balancing the mass in Reaction 1 has been omitted. For the range of carbon atoms envisioned and the metathesis conditions for this invention, ethylene will exist as a gas and the desired valuable metathesis product will be a liquid.

[0024] According to the well-known textbook entitled "Olefin Metathesis and Metathesis Polymerization" by Ivin and Mol, Academic Press, 1997, PP. 1, "The metathesis reactions are generally reversible and, with the right catalyst system, equilibrium can be attained in a matter of seconds, even with substrate/catalyst ratios of 104; a truly remarkable reaction." Thus it is seen that metathesis reactions are catalytic reactions and, very importantly, equilibrium limited. This means that reaction is typically not complete but results in a final equilibrium mixture of reactants and

products. Therefore, in the case of Reaction 1, for this invention the ethylene by-product (which is gas) is removed from the reaction vessel. The ethylene may be removed by use of an inert gas purge, by operating the reaction at reduced pressure, or a combination of vacuum and inert gas purge to remove the ethylene gas. For this purpose, inert gas is defined as a gas that does not participate in the metathesis reactions. Suitable inert gases include, but are not limited to, nitrogen, steam, carbon dioxide, straight chain alkanes (e.g. methane, ethane, propane, butane, etc.) and branched alkanes (e.g. isobutane, etc.). Nitrogen is the preferred purge gas. As will be seen in the Examples section of this application, removal of the ethylene serves to shift the reaction equilibrium to favor the desired product, which drives the reaction to completion. In practice, this operation also serves as means to separate the desired liquid metathesis product from the ethylene by-product. Removal of the ethylene and driving the reaction to completion also obviates the need for recycle of un-reacted product for further processing.

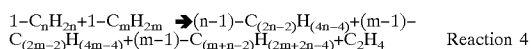
[0025] For metathesis understanding purposes only, it is useful to envision that the linear feed alpha-olefin molecule is "cut" into two fragments at the double bond, a one-carbon fragment and an (n-1) carbon fragment. Again, for further understanding only, it may be envisioned that the one carbon fragment can recombine with an (n-1) carbon fragment forming a double bond at the combination point and regenerating the original feed linear alpha-olefin molecule. An alternative and desired possibility is for two (n-1) fragments to combine forming the desired metathesis internal olefin. When two one carbon fragments combine, ethylene is formed.

[0026] Some further insight into self-metathesis may be gained by reviewing specific examples. Reaction 2 and Reaction 3 below indicate the self-metathesis of linear (normal) 1-decene to 9-octadecene and linear (normal) 1-nonene to 8-hexadecene respectively.



[0027] Again, for the sake of simplicity, balancing the mass in Reactions 2 and 3 has been omitted. It is obvious from these two examples that the internal olefin formed from self-metathesis of a linear alpha-olefin always has an even number of carbon atoms regardless of whether an odd or even number carbon atom alpha-olefin is self-metathesized. Also, the double bond is always located exactly in the center of the internal olefin formed, i.e., after carbon atom 9 for C_{18} and after carbon atom 8 for C_{16} .

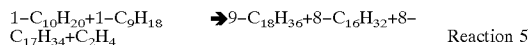
[0028] As previously mentioned, the metathesis feed may be comprised of two or more linear alpha-olefins. Applicants refer to this process as cross-metathesis. Reaction 4 below indicates the situation that would prevail for cross-metathesis when the feed comprises two linear alpha-olefins.



[0029] As in the previous reactions, the mass in Reaction 4 is not balanced for the sake of simplicity. In Reaction 4, n and m are integers in the range of 4 to 22, are not equal to each other, and m has a lower value than n. As was the case for self-metathesis, C_2H_4 is ethylene. For the range of carbon atoms envisioned and the metathesis conditions of this invention, ethylene will exist as a gas and the desired

cross-metathesis products will be liquid. In practice, the ethylene gas is easily removed serving to drive the reaction to completion and also serving as means to separate the desired and more valuable liquid metathesis products from the ethylene by-product.

[0030] A specific example, showing the cross metathesis of 1-decene and 1-nonene, is given by Reaction 5.



[0031] As before, the mass is not balanced in Reaction 5. The cross-metathesis of 1-decene with 1-nonene yields some 9-octadecene and some 8-hexadecene as was the case for the separate self-metathesis of these two linear alpha-olefins. However, a new product, 8-heptadecene (C_{17}), is also formed by combination of an 8-carbon atom fragment with a 9-carbon atom fragment. Because 8-heptadecene has an odd number of carbons atoms, it is not possible for the double bond in this internal linear olefin to be at the very center of the molecule.

[0032] Cross metathesis of feeds comprising three different alpha-olefins would lead to production of six liquid internal olefin metathesis products plus ethylene. In a similar manner, it can be calculated that cross metathesis of feeds comprising four different alpha-olefins would lead to production of ten liquid internal olefin metathesis products. Cross metathesis of feeds comprising two, three, or more than three different alpha-olefins leading to wide varieties of liquid internal olefin metathesis products is also envisioned to be within the scope of this invention.

[0033] Having now considered cross metathesis in more detail, it is necessary to briefly reconsider self-metathesis. This will be done by further consideration of the self-metathesis of 1-decene as given by Reaction 2 where the desired product is $9-C_{18}H_{36}$ and the by-product is ethylene. The (unwanted) presence of 2-decene subjected to metathesis will provide for the presence of some C_8 and some C_2 molecule fragments. These unwanted fragments could combine with some of the many C_9 fragments present to form $8-C_{17}H_{34}$ and $2-C_{11}H_{22}$. This side reaction is undesirable and can be prevented, or at least minimized, by reducing the amount of 2-decene present. The 2-decene may be present in the metathesis reactor because it was present in the metathesis feed. Therefore, feed quality and purity of the 1-decene of Reaction 2 may be important for certain applications. The second source of 2-decene in the metathesis reactor is from the isomerization of 1-decene to 2-decene. The presence of 2-decene from isomerization may be controlled by selection of the proper metathesis catalyst formulation to one which prohibits the isomerization of 1-decene to 2-decene. In part, this may be accomplished by choice of the metathesis catalyst support. The support should have only minimal acidic sites so as discourage 1-decene isomerization. Processes for making very low or acidic neutral alumina support are well known in the art. Applicants have found that use of gamma-alumina as the support provides good results. Often, the same objective may be achieved by making metals of Groups VIA, VIIA, and their oxides part of the metathesis catalyst system.

[0034] The self and cross metathesis of the C_4 to C_{22} linear alpha-olefins may be conducted in batch or continuous mode. The metathesis may be done in single reactors, plural reactors in series or parallel, and via up flow or down flow

of materials. Generally the metathesis is conducted via a fixed bed catalyst process with heterogeneous catalyst. The catalyst composition will comprise about 2 to about 20 percent by weight catalyst metal or metal oxide and the remainder will be comprised of support. The preferred support is alumina. Especially preferred is gamma alumina. The preferred weight percent catalyst metal or metal oxide is from about 5 to 15 weight percent, and especially preferred is about 10 weight percent catalyst metal or metal oxide and about 90 weight percent support. The suitable metathesis catalyst metal or metal oxide catalysts include any transition metal or metal oxide from the Groups VIB (Cr, Mo, W), VIIB (Mn, Tc, Re), and VII (Ru, Co, Pt, Pd, Fe, Ni, Ir, Os) or any combination of them. Preferred metal or metal oxide catalysts are Re, W, Mo, and Co, or combinations of them. Especially preferred is Re and/or Re oxides.

[0035] The metathesis is carried out under relatively mild reaction conditions in an effort to prevent or at least minimize isomerization of the alpha-olefin feed and metathesis products once formed. Generally the reactor temperature will be maintained in the range of about 0° C. to about 150° C. The preferred reactor temperature is in the range of about 20° C. to about 110° C. The residence time in the reactor will run from as little as about fifteen minutes to as much as about 12 hours. The preferred residence time in the reactor is from about 0.5 hour to about 6 hours.

[0036] As in any other process, the desired effect for the self and cross metathesis is a high conversion rate and a high rate of selectivity to the desired metathesis product or products. The by-product of the metathesis reactions is ethylene. Ethylene exists as a gas and the desired metatheses products are liquid at the reaction conditions recited above. Therefore, it is a relatively simple process to separate the desired liquid product from the gaseous by-product, ethylene. Removal of the gaseous by-product ethylene helps to drive the metathesis reaction to completion. Removal of the ethylene gas may be accomplished by continuously purging the reactor with an inert gas, such as nitrogen. The reaction pressure is generally maintained at about one atmosphere, but reactor pressures in the range of 0.1 to about 5.0 atmospheres are suitable. An alternative method for enhanced separation of ethylene from the desired liquid metathesis is to operate the reaction at pressures below 1.0 atmosphere so as to accelerate the removal of the ethylene.

[0037] The degree of selectivity of the metathesis reaction depends, at least in part, on the purity of the alpha-olefin feed provided. The linear alpha-olefin feed was previously defined. The feed covers olefins having in the range of about 4 to about 22 carbon atoms. As previously noted, the nature and purity of the feed varies, to some extent, based on the carbon count of the olefin in the metathesis feed. Especially unwanted in the feed are excess amounts of branched (non-linear) alpha-olefins that will lead to production of branched metathesis products. Also, excess amounts of internal olefins in the metathesis feed will lead to mixed metathesis products and also to short carbon chain by-products other than ethylene. The branched and internal olefins in the feed may be a result of isomerization of the feed during the metathesis. The short carbon chain by-products may not be entirely gaseous which will affect conversion rate as well as product purity. Another factor in determining selectivity is the mild reaction conditions employed. It is important to minimize isomerization of the

liquid metathesis product prior to removal from the reactor. This undesired isomerization may take the form of migration of the double bond to a position further from the center of the internal olefin molecule. Another undesired isomerization is branching of the linear internal olefins formed by the metathesis reaction. Yet another isomerization of the metathesis product to be avoided is formation of tri-substituted olefins. Thus, in addition to mild conditions, it is also extremely important to select a metathesis catalyst that is essentially inactive in terms of isomerization of the liquid metathesis products or the feed.

[0038] The linear internal olefin metathesis products are very valuable liquids. Well fluid base oils comprised of these liquids have pour points of about 0° C. and are environmentally friendly in that they exhibit very low toxicity toward marine life. While not wishing to be bound by theory, applicants speculate that the low pour point temperature of well fluids comprising these liquids may be due to the extreme and deep internal olefin isomers produced by the metathesis process, to the lack of branching, and also due to the extreme homogeneity of the product. Applicants have no ready answer to the reason for their low toxicity to marine life. It is now recognized that unsaturated fats having excess trans isomer may pose a threat to humans at least equal to that posed by saturated fats. Perhaps the distribution of cis and trans isomers produced by the metathesis process may also explain, at least in part, the reason for the low toxicity of these fluids to marine life.

[0039] In practice, formulations of well fluid base oils comprising these liquid metathesis products will be further comprised of many additional substances including typical well fluid base oil additives and additive packages. In certain instances, and sometimes simply for the sake of convenience or available materials or as a means to reduce the cost of the base oils, other materials may contribute a portion of formulations comprising these base oils. Additional and/or optional materials may be included only to the extent that the resulting base oils maintain their two salient features of (1) pour point temperatures in the range of about 0° C., or lower and (2) low toxicity to marine life.

[0040] Other components of the well fluid base oils comprising the liquid metathesis products may include linear alpha-olefins in the range about 8 to 20 carbon atoms, mixtures of these linear alpha-olefins, linear internal olefins in the range of about 8 to 20 carbon atoms, mixtures of these internal olefins, and mixtures involving at least two of the preceding. If present as a component in the well fluid base oils, the linear alpha-olefins may be formed by any known process (including dehydration of normal alcohols) and their method of production forms no part, per se, of the present invention. If present as a component in the well fluid base oils, the linear internal olefins may be formed by any known process and their method of production forms no part, per se, of the present invention. Known processes for production of internal linear olefins is intended to include metathesis products of olefins other than as disclosed above and also is intended to include olefins which originated from any known process. Such known processes include but are not limited to the following: (1) dehydration of alcohols, (2) dehydrohalogenation of halogenated hydrocarbons, (3) cracking of aliphatic hydrocarbons, (4) dehydration of alkanes or paraffinic hydrocarbons including hydroforming reactions, (5) conversion of esters to alcohols and acids followed by

dehydration reactions, (6) oligomerization of lower carbon number (e.g., ethylene, propylene, butene, pentene, hexene) olefins, and (7) Fischer-Tropsch reactions (catalytic reactions of carbon monoxide and hydrogen via iron or cobalt containing catalysts).

[0041] The liquid metathesis products also find utility as precursors to surfactants. Upon addition of a polar group (e.g., sulfonate, sulfate, acid, amine, amine oxide, oxide, etc.) via known chemical processes to the deep internal olefin liquid metathesis products, a surfactant with enhanced oil solubility emerges. The enhanced oil solubility is with respect to addition of a similar polar group to an alpha-olefin or to a conventionally, internally isomerized linear alpha-olefin. The enhanced oil solubility of the polarized liquid metathesis products allow use of the surfactant in lower concentration to effectively lower the interfacial surface tension of the oil as well as improve the surfactant's emulsifying and dispersant properties. Such benefits are useful in light and heavy-duty surfactant applications. Additionally, these surfactants should be able to absorb oil from a marine oil spill without wave action or agitation.

[0042] The valuable liquid metathesis products also find utility as a precursor component of lube oils. Typically, the liquids products of the metathesis would be hydrogenated and then used as a component of lube oils. The valuable liquid metathesis products also find utility as a precursor component and/or as a component in the production of lube oil additives.

[0043] The liquid metathesis products also find utility as a precursor to alkenyl succinic anhydride (ASA) compounds. ASA compounds are used extensively in the papermaking industry as a paper-sizing additive for improving properties of paper, including fine paper and gypsum board. Commercial sizing agents based on ASA compounds are typically prepared from the reaction products of C_{14} to C_{22} olefins and maleic anhydride. The properties of the olefins used in this reaction have a major influence on the sizing performance of the resulting ASA compounds in the paper sizing process. Specifically, ASA compounds prepared from maleic anhydride and C_{16} internal olefins, C_{18} internal olefins and mixtures of C_{16} and C_{18} internal olefins are among the more preferred ASA compounds. The liquid metathesis products provide exceptional performance when used in the formation of ASA compounds. The unique structural characteristics of the liquid metathesis products such as the amount and type of internal olefins impart properties to the resulting ASA that provide excellent sizing performance.

[0044] The liquid metathesis products also find utility in lubricant compositions as metalworking fluids, cutting oils, and quench oils. The lubricity and physical properties of the liquid metathesis products are useful characteristics in lubricating oil compositions for metal fabrication such as cold metal and alloy metal forming applications and other metalworking operations such as blanking, bending, stamping, rolling, forging, punching, pressing, forming and drawing processes. The high boiling point of some liquid metathesis products such as those formed by the self-metathesis of 1-decene (boiling point 162°C .) or those forming compounds with higher carbon numbers provide a useful feature by allowing a higher maximum workable die temperature. The low toxicity and environmentally friendly characteristics of the liquid metathesis products may be useful in

metalworking fluid applications requiring direct food contact. As a component of a metalworking fluid, the liquid metathesis products may assist in the cutting, grinding, or forming of metal and function to improve the lifetime and fabrication precision of the tool and improve productivity of the process.

[0045] In addition to specific applications for the liquid metathesis products made by the process disclosed above, the disclosed metathesis process also provides a convenient method for the manufacture of specialty linear internal olefins from linear alpha-olefins essentially on a made to order, custom basis. For example, suppose a need existed for manufacture of the rather unusual compound, linear internal olefin 3-hexadecene ($3-C_{16}H_{32}$). This compound could easily be prepared in high purity by the metathesis process disclosed above. According to Reaction 4, which governs cross metathesis of two alpha-olefins, it would be necessary to cause a feed comprising linear 1-butene ($1-C_4H_8$) and linear 1-tetradecene ($1-C_{14}H_{28}$) to cross metathesis under metathesis reaction conditions. According to Reaction 4, three metathesis products would be formed in addition to by-product gaseous ethylene. These three metathesis products would be 3-hexene ($3-C_6H_{12}$), the C_{26} internal olefin 13- $C_{26}H_{52}$, and also 3-hexadecene ($3-C_{16}H_{32}$), the desired internal olefin. The gaseous ethylene by-product is separated from the three liquid metathesis products. The separation may be easily accomplished by purging with an inert gas. Removal of the gaseous by-product ethylene also helps to drive the reaction to further completion. The desired product, 3-hexadecene, may be easily isolated and purified from the other liquid products by distillation or other separation and purification processes well known in the art. Other liquids present, if any, may optionally be recycled as feed or otherwise recovered.

[0046] In a similar manner, the linear internal olefin 5-hexadecene would be prepared from cross metathesis of 1-hexene with 1-dodecene ($1-C_{12}H_{24}$). The linear internal olefin 4-hexadecene would be prepared from cross metathesis 1-pentene with 1-tridecene ($1-C_{13}H_{26}$). The linear internal olefin 6-hexadecene would be prepared from cross metathesis 1-heptene ($1-C_7H_{14}$) with 1-undecene ($1-C_{11}H_{22}$). The linear internal olefin 7-hexadecene would be prepared from cross metathesis 1-octene ($1-C_8H_{16}$) with 1-decene ($1-C_{10}H_{20}$). The linear internal olefin 8-hexadecene would be prepared from self-metathesis of 1-nonene. Thus, all of the deep internal linear hexadecene olefins (3 or 4 or 5 or 6 or 7 or 8-hexadecene) could be prepared via the metathesis process disclosed above. In a similar manner, most of the internal tetradecenes, pentadecenes, heptadecenes, octadecenes, etc. could be prepared by self or cross metathesis of the appropriate linear alpha-olefin feed as disclosed. The range of specialty linear internal olefins that can be prepared is extremely wide. The substance linear 9-tricosene ($9-C_{23}H_{46}$) could be prepared by cross metathesis of 1-decene with 1-pentadecene. The substance linear 15-triacontene ($15-C_{30}H_{60}$) could be prepared from self-metathesis of 1-hexadecene.

[0047] Surprisingly, applicants have found that the pour point temperatures of well fluid base oils comprising the liquid metathesis products could be lowered by an additional 15°C . to 40°C . by further isomerization of the liquid metathesis products. In many instances, only partial isomerization may be necessary to achieve the benefit of pour point

temperature depression. This pour point temperature improvement is obtained without sacrifice of the excellent toxicity properties of the well fluid base oils comprising the metathesis liquids. In practice this is achieved by subjecting the metathesis product to internal isomerization conditions in the presence of an internal isomerization catalyst. Generally the feed for the isomerization step will be comprised of the metathesis product in the range of at least about 10 weight percent to about 100 weight percent of the isomerization process feed. Preferably the isomerization feed will be comprised of metathesis product in the range of about 50 weight percent to about 100 weight percent. Most preferably the isomerization feed will be comprised of metathesis product in the range of about 70 weight percent to about 90 weight percent. Other components of the isomerization feed may include linear alpha-olefins in the range about 8 to 20 carbon atoms, mixtures of these linear alpha-olefins, linear internal olefins in the range of about 8 to 20 carbon atoms, mixtures of these internal olefins, and mixtures involving at least two of the preceding. If present in the isomerization feed, the linear alpha-olefins may be produced by any known process (including dehydration of normal alcohols) and the process for producing them forms no part, per se, of the present invention. If present in the isomerization feed, the linear internal olefins may be produced by any known process and the process for producing them forms no part, per se, of the present invention. Known processes for production of internal linear olefins is intended to include metathesis processes other than as disclosed above and also is intended to include olefins which originated from dehydration of alcohols.

[0048] The isomerization conditions employed for the feed comprising the metathesis process liquids are also rather mild. Typical temperatures employed in the isomerization reactor are in the range of about 50 to about 350° C. The preferred temperature range is from about 100 to about 300° C. The isomerization catalyst is selected from the group consisting of any solid catalysts containing Bronsted and/or Lewis acid sites. These catalysts include the heterogeneous catalysts (or combination of at least two of them) such as commercially available or developmental catalysts, HY-zeolite, H-ZSM-5, Theta-1 (or ZSM-22), supported PMA (phosphomolybdic acid), supported HPW (phosphotungstic acid), pure or halogenated alumina or magnesia, silica-alumina, Group VIII metals on alumina, phosphate-containing alumina or magnesia, Amberlyst (ion-exchange resin, A-35D or A-15D), sulfated zirconia, Nafion, SAPO-11, SAPO-34, etc. The preferred isomerization catalysts are alumina, H-ZSM-5, Nafion, and Theta-1. Pressures employed during the isomerization range from about 1 atmosphere to about 50 atmospheres.

[0049] Both the metathesis and isomerization portions of the process can be practiced with fixed bed reactors, via up or down flow mode, with one reactor or multiple reactors, in cyclic mode (e.g. one or more in operation, one in purging, one in regeneration), and with one-pass through or with recycle. Regeneration of the catalyst can be accomplished by using dry air or diluted air to burn off coke, followed by re-oxidation of the metal in the metathesis catalyst followed by purging with inert gases. The regeneration off-gas can also be recycled to save cost.

[0050] A major use for these isomerized internal olefins is as a component in formulations of well fluid base oils. When

well fluid base oils are formulated comprising the product of the isomerization process disclosed above, it is found that the well fluid base oils retain, and often improve, their salient property of low toxicity to marine life. However, the pour points of the resulting well fluid base oils has been lowered by as much as about 40° C. to absolute pour point temperatures of about -36° C. In practice, formulations of well fluid base oils comprising these internal isomerization products will be further comprised of many additional substances including typical well fluid base oil additives and additive packages. In certain instances, sometimes simply for the sake of convenience or available materials or as a means to reduce the cost of the base oils, other materials may contribute a portion of formulations comprising these base oils. Additional and/or optional materials may be included only to the extent that the resulting base oils maintain their two salient features of (1) pour point temperatures in the range of about -15° C. and as low as -36° C. and (2) low toxicity to marine life.

[0051] In one major embodiment, this invention is directed to a process for production of valuable liquid products suitable for use as at least one component in low pour point temperature and low toxicity well fluid base oils comprising the steps of:

[0052] (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,

[0053] (ii) subjecting said feed to metathesis conditions in the presence of a metathesis catalyst so as to form valuable liquid metathesis products and gaseous ethylene as a by-product,

[0054] (iii) separating the valuable liquid metathesis products from the gaseous ethylene so as to drive the reaction to completion and permit recovery of the valuable liquid metathesis products,

[0055] (iv) optionally, further purifying the liquid metathesis products from step (iii), and

[0056] (v) subjecting a feed comprising about 10 to 100 weight percent of the product selected from step (iii), step (iv) and mixtures thereof to isomerization conditions in the presence of an isomerization catalyst.

[0057] In another embodiment, this invention is directed to a process for production of valuable liquid products suitable for use as at least one component in low pour point temperature and low toxicity well fluid base oils comprising the steps of:

[0058] (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,

[0059] (ii) subjecting said feed to metathesis conditions in the presence of a heterogeneous supported metathesis catalyst so as to form valuable liquid metathesis products and gaseous ethylene as a by-product,

[0060] (iii) separating the valuable liquid metathesis products from the gaseous ethylene so as to drive the reaction to completion and permit recovery of the valuable liquid metathesis products,

[0061] (iv) optionally, further purifying the liquid metathesis products from step (iii), and

[0062] (v) optionally, subjecting a feed comprising about 10 to 100 weight percent of the product selected from step (iii), step (iv) and mixtures thereof to isomerization conditions in the presence of an isomerization catalyst.

[0063] In yet another preferred embodiment, this invention is directed to a process for production of specialty linear deep internal olefins comprising the steps of:

[0064] (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,

[0065] (ii) subjecting said feed to metathesis conditions in the presence of a heterogeneous supported metathesis catalyst so as to form valuable liquid specialty linear internal olefins and gaseous ethylene as a by-product,

[0066] (iii) separating the valuable liquid metathesis products from the gaseous ethylene so as to drive the reaction to completion and permit recovery of the valuable liquid metathesis products,

[0067] (iv) optionally, further purifying the liquid specialty internal olefins metathesis products from step (iii).

EXAMPLES

Preparation of Catalysts A, B and C

[0068] Catalysts used in all examples, except as noted, were prepared as follows:

[0069] Catalyst A: A standard nominal 10 weight percent rhenium- γ -alumina (gamma-alumina) catalyst was prepared by completely dissolving NH_4ReO_4 in water at 85° C. The NH_4ReO_4 solution of NH_4ReO_4 was used to wet-impregnate γ -alumina powder (80-100 mesh). This was followed by drying with air at 200° C. for about 120 minutes, calcining in air at 525° C. for about 180 minutes, and finally cooling under N_2 to room temperature.

[0070] Catalyst B: A standard nominal 10 weight percent rhenium- γ -alumina (gamma-alumina) catalyst was prepared by completely dissolving NH_4ReO_4 in water at 85° C. The solution of NH_4ReO_4 was used to wet-impregnate γ -alumina quadralobe extrudate (0.1 cm (0.04 inch) quadralobe extrudate). A quadralobe extrudate is only one of several suitable choices. The purpose and intent is to maximize the surface area of the catalyst and still maintain its crush strength. Other suitable catalyst extrudate shapes would include trilobe, hollow cylinder, doughnut, star, and CDS. The wet-impregnated extrudate was then dried with air at 200° C. for about 120 minutes, calcined in air at 525° C. for about 300 minutes, and finally cooled to room temperature under nitrogen gas.

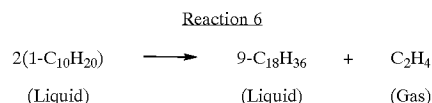
[0071] Catalyst C: Prepared in the same manner as Catalyst A, except that boric acid was also dissolved in the NH_4ReO_4 solution so as to comprise 2 weight percent of the final catalyst formulation.

[0072] Catalyst handling was conducted in a dry box where nitrogen was used as a blanket and oxygen level in the dry box was always maintained well below 100 ppm. The 1-decene metathesis reactions were conducted in glass reactors, which typically contained 3 grams of Catalyst A with 40 ml (or 30 grams) of decene liquid resulting in 0.1 to 1 weight ratio of Re catalyst to 1-decene feed. Untreated decene was the feed received as 1-decene from the BP Pasadena, Tex. LAO plant. Treated 1-decene was obtained by treating the BP Pasadena, Tex. 1-decene with a basic alumina powder in order to remove impurities such as water, alcohols, and oxygenated compounds. Before treating the 1-decene feed, the basic activated alumina, (Aldrich 19,944-3) was first treated in a Muffle furnace (in air) at 250° C. for 16 hours. The 1-decene pretreatment then was conducted under nitrogen blanketing.

Examples 1-5

[0073] In a glass slurry reactor a magnetic stirrer constantly agitated the reactor mixture so the 1-decene liquid and Catalyst A were in good contact during the one-hour reaction. Mineral oil bath provided homogeneous heating to the reactor, typically set at 60° C. A septum on top of the reactor prevented the reaction mixture from contacting ambient air or moisture. For non-equilibrium operations during the reaction, nitrogen was introduced into contact with the reaction mixture through a syringe. A mass flow meter was always used to monitor the flow rate of the reaction off-gas in ml/min. Gas chromatography was used to analyze the 1-decene feed and the reaction products. Percent conversion of 1-decene was calculated by subtracting the weight % 1-decene in the product mixture from that in the feed, dividing by the amount in the feed, and then multiplying by 100. Selectivity was calculated by dividing the sum of the weight of C16, C17 and C18 olefins in the product mixture by the total weight of all the compounds present (other than 1-decene) in the product mixture, and then multiplying by 100. The ethylene gas was not included in the selectivity calculation.

[0074] The objective was to maximize the main, and desired, metathesis reaction (as given by Reaction 6) at 60° C. with Re catalysts.



[0075] Two types of side, and undesired, reactions were also observed: (I) isomerization of 1-decene, which reduces selectivity, and (II) the reaction of ethylene with other olefins, which reduces conversion and selectivity.

[0076] (I) Isomerization reactions can occur because of the acidic sites on the catalyst surface to form internal decene isomers prior to metathesis. For example, isomerization of 1-decene forms 2-decene, which can then react with the 9-octadecene to form 2-C₁₁H₂₂ and 8-C₁₇H₃₄ internal olefins. Isomerization of 1-decene and 2-decene also forms 3-decene, which can react with 9-octadecene to form 3-C₁₂H₂₄ and 7-C₁₆H₃₂ internal olefins. If present, 4-decene can react with 9-octadecene to form 4-C₁₃H₂₆ and 6-C₁₅H₃₀.

internal olefins. The 2.5 weight % branched compounds in the 1-decene feed such as the vinylidenes, 2-ethyl-octene-1 (2EO1) and 2-butyl-hexene-1 (2BH1), are readily catalytically isomerized into their respective trisubstituted species. Four compounds are formed by the isomerization of 2EO1. These are trans and cis forms of 3-methyl-3-nonene and trans and cis forms of 3-methyl-2-nonene. Four compounds are formed by the isomerization of 2BH1. These are trans and cis forms of 5-methyl-5-nonene and trans and cis forms of 5-methyl-4-nonene.

[0077] These unwanted isomerization reactions are difficult to control except by using catalyst containing minimal acidic sites. The catalysts used for these examples were supported on a non-acidic (i.e., neutral) alumina support, thereby causing only minimal isomerization of 1-decene.

[0078] (II) Small amount of dissolved ethylene gas formed by the main self-metathesis reaction can react with any olefins to form other olefin molecules. For example, ethylene can react catalytically with any decene isomers such as internals and vinylidenes to cleave olefins at the double bond to form olefins with different carbon numbers. Although ethylene exists in very small amounts, its reactions reduce selectivity and conversion of the main reaction.

[0079] The use of nitrogen gas to purge the gaseous and unwanted ethylene by-product also serves to drive the reaction to completion. Examples 1-5 described in Table 1 below serve to show this inventive aspect for the self metathesis of 1-decene using Catalyst A with treated 1-decene feed at a reactor temperature of 60° C., reactor residence time of 60 minutes, and a Re to 1-decene ratio of 0.1

TABLE 1				
Examples 1-5 Self-metathesis of 1-decene				
Ex. No.	N ₂ Purge	Feed Volume	Conversion Percent	Selectivity Percent
1	No	40 ml	77.1	92.2
2	No	30 ml	79.4	91.1
3	No	200 ml	77.0	91.6
4	Yes	40 ml	90.7	94.7
5	Yes	40 ml	93.4	95.8

[0080] These data show that, with Catalyst A, both conversion and selectivity in the self-metathesis of 1-decene are improved by purging the reaction mixture with nitrogen. The percent conversion and the selectivity percent are calculated as recited above.

[0081] The use of nitrogen gas to purge the gaseous and unwanted ethylene by-product also serves to drive the reaction to completion when used with a modified Catalyst A. Modified Catalyst A was improved over Catalyst A by lengthening the impregnation time and using 70-100 mesh γ -alumina. Examples 6-7 described in Table 2 below serve to show this inventive aspect for the self metathesis of 1-decene using modified Catalyst A with treated 1-decene feed at a reactor temperature of 60° C., reactor residence time of 60 minutes, and a Re to 1-decene ratio of 0.1

TABLE 2				
Examples 6-7				
Ex. No.	N ₂ Purge	Feed Volume	Conversion Percent	Selectivity Percent
6	No	40 ml	75.2	93.6
7	Yes	40 ml	94.2	97.8

[0082] These data show that, with modified Catalyst A, both conversion and selectivity in the self-metathesis of 1-decene are improved by purging the reaction mixture with nitrogen. The percent conversion and the selectivity percent are calculated as recited above.

[0083] As comparative examples, Applicants tested Catalyst C for self-metathesis of 1-decene. Recall that Catalyst C is the same as Catalyst A except that it also is comprised of 2 weight percent boric acid. Catalyst C, with its acidic sites, would be predicted to be a better isomerization catalyst than Catalyst A. Comparative Examples 7-10 in Table 3 below serve to show that a use of a nitrogen purge no longer improves conversion and selectivity for the self metathesis of 1-decene using acid site Catalyst C with treated 1-decene feed at a reactor temperature of 60° C., and a Re to 1-decene ratio of 0.1.

TABLE 3					
Examples 7-10 Catalyst C-self-metathesis of 1-decene					
Ex. No.	N ₂ Purge	Feed Volume	Reaction Time	Conversion Percent	Selectivity Percent
7	No	40 ml	30 min.	75.3	24.8
8	Yes	40 ml	30 min.	77.0	25.9
9	No	40 ml	60 min.	91.0	26.3
10	Yes	40 ml	60 min.	89.9	27.5

[0084] It can be seen that with 30 minutes reactor time (Ex. 8) and 60 minutes reactor time (Ex. 10), the conversion level was essentially not affected by the nitrogen purge when using an acid catalyst. Applicants believe this is because of the high isomerization activity of Catalyst C. For further understanding, a gas chromatography analysis of the feed and reaction mixture is shown for Examples 9 and 10 in Table 4 below.

TABLE 4			
Examples 9 & 10 GC Analysis of Feed and Products			
Example No.	9 & 10	9	10
Analysis of Catalyst	1-Decene Feed	Reaction Mixture C	Reaction Mixture C
N ₂ Purge		No	Yes
Material Analyzed	1-Decene Feed wt %	Reaction Mixture wt %	Reaction Mixture wt %
Lights (<C8)		0.51	0.666
C ⁸		0.44	2.077
C ⁹	0.98	0.34	0.87
C10 unk. 1	0.11	0.095	0.088
C10 unk. 2	0.04	0.044	0.041
Butyl Branched	0.59	0.166	0.15

TABLE 4-continued

Examples 9 & 10			
GC Analysis of Feed and Products			
Example No.	9 & 10	9	10
Ethyl Branched	0.89	0.28	0.21
1-Decene	94.88	8.71	9.74
3, 4, & 5-C ⁻ 10	0.12	16.49	13.25
Decane	0.29	0	0
C-2-Decene	1.08	24.03	21.04
T-2-Decene	0.59	23.02	21.29
C11-unk. 1		0.77	3.00
C11 unk. 2		0.30	0.81
C ⁻ 12		0.21	0.32
C ⁻ 13		0.089	0.194
C ⁻ 14		0.082	0.21
C ⁻ 15		0.217	0.40
C ⁻ 16		0.956	1.63
C ⁻ 17		1.39	3.17
9-C ⁻ 18		21.764	20.624
C ⁻ 18 other		0.051	0.18
C ⁻ 19+		0.04	0.031
Total, %	99.6	99.99	99.99
Selectivity to C16-18, %		26.3	27.5
Conversion, %		91.0	89.9

[0085] In Table 4, unk. Indicates an unknown substance that was found and C⁻ indicates an olefin. At 60 minutes residence time, (Examples 9 and 10), the conversion level was essentially not affected by nitrogen purging yet the selectivity to C16-18 was unusually low. This was due to the high isomerization activity of 1-decene, as shown in the Table 4. Note that the combined C₁₀ internals, (cis and trans 2-decene) formed was over 55% with nitrogen purging and over 63% with no purging. Since the isomerization reactions

of 1-decene are undesired reactions that do not produce ethylene gas, the total conversion and selectivity cannot be improved by purging with nitrogen when using an acid (isomerizing) catalyst.

Examples 11-21

[0086] When subjected to isomerization conditions in the presence of an olefin isomerization catalyst, the metathesis liquids obtained using Catalyst A or Catalyst B acquire some unique and especially salient properties. The data of Table 5 show the unique properties obtained by using Catalyst B extrudates for self-metathesis of 1-decene followed by isomerization of the self-metathesis product of 1-decene. The metathesis was conducted using a continuous flow reactor with nitrogen gas flowing concurrently with the 1-decene feed. The ratio of nitrogen purge flow to 1-decene was 1.5 g nitrogen to 1 g 1-decene. The beginning reactor temperature was 40° C., the WHSV was 1, and a pressure of 1 atmosphere was employed. The initial conversion rate for fresh catalyst was always 90% with high selectivity (95-97% without accounting for ethylene). As the catalyst deactivates the conversion fell to ~75% at which time reactor temperature was increased to raise conversion rate but selectivity was always maintained at about the the same level. The metathesis reactor product was collected and then distillation was conducted at 100-mm Hg pressure to separate the 9-octadecene product from unconverted 1-decene feed. For Examples 11 to 21, the specific isomerization conditions employed were dependent on the isomerization catalyst deployed and are as listed in Table 5 below.

[0087] For purposes of comparison, Table 6 shows some physical properties of 1-octadecene, and the 9-octadecene produced by self-metathesis of 1-decene (Example 11). It can be seen that the boiling point of 9-octadecene is higher and the melting point is lower which makes 9-octadecene a liquid over a very long temperature range.

TABLE 5

Examples 11-21											
Properties of 9-octadecene and isomerized 9-octadecene											
Example	11	12	13	14	15	16	17	18	19	20	21
Species	9-C18	C18IO	C18IO	C18IO	C18IO	C18IO	C18IO	C18IO	C18IO	C18IO	C18IO
Isomerization Catalyst	N/A	Al ₂ O ₃	Al ₂ O ₃	Theta-1	Theta-1	Theta-1	PMA /TiO ₂	PMA /TiO ₂	PMA /TiO ₂	HZSM5 (T2559)	A-35D
Isomerization Temp. ° C.	N/A	220	300	200	220	220	200	220	220	220	100
Isomerization Time, hours	N/A	2	1	2	1	2	2	1	2	2	2
Vinyl, wt %	0.0	0.0	0.0	0.0	0.0	0.51	0.80	0.79	0.67	0.5	0.54
Internal, wt %	99.37	96.3	99.74	65.9	52.6	41.1	89.2	90.6	91.4	91.3	63.6
Trisubs, wt %	0.61	2.9	2.3	33.2	46.2	55.9	9.8	8.5	7.7	7.9	35.5
Vinylidenes, wt %	0.02	0.1	0.0	0.9	1.27	2.5	0.21	0.17	0.21	0.3	0.37
CH ₃ /olefin	2.02	2.1	2.1	2.6	3.1	3.6	2.15	2.13	2.2	2.11	3.34
CH ₂ /olefin	13.74	14.1	14.2	14.6	15.6	16.1	14.1	14.0	14.2	13.9	19.9
C _{ave} /olefin	17.76	18.2	18.4	19.3	20.7	21.7	18.25	18.13	18.4	18.0	25.2
Melt. Pt., ° C.	-30.5										—
Pour Pt., ° C.	0	0	-18	-21	-30	-36	-12	-12	-15	-15	-15
V _g 0° C., cSt	—	—	9.6	11.9	13.7	17.2	10.6	10.4	10.6	10.1	26.0
V _g 4.4° C., cSt	—	—	8.4	10.2	11.8	—	9.3	9.1	—	—	—

TABLE 5-continued

Example	Examples 11-21										
	Properties of 9-octadecene and isomerized 9-octadecene										
	11	12	13	14	15	16	17	18	19	20	21
V, 40° C., cSt	3.4	3.6	3.5	4.0	4.4	5.0	3.7	3.7	3.7	3.6	7.0
V, 100° C., cSt	1.40	1.46	1.43	1.56	1.66	1.80	1.49	1.49	1.49	1.45	2.29
Trans/Cis	78/22	75/25	69/31								

Keys to Table 5:
(1) 9-C18 is 9-octadecene; C18IO is isomerized 9-octadecene; (3) Vinyl wt % is the amount of alpha-olefin, i.e., $\text{CH}_2=\text{CHC}_{16}\text{H}_{33}$ as determined by NMR; (4) Internal wt % is the amount of internal olefin where double bond is not in alpha position as determined by NMR, (one hydrogen on each double bond carbon atom, cis or trans); (5) Trisubs. wt % is the amount of trisubstituted internal olefin, i.e., only one hydrogen total on both double bond carbon atoms as determined by NMR; (6) Vinylidenes wt % is the amount of vinylidene olefins (two hydrogens on one of the double bond carbon atoms and two alkyl groups on the other double bond carbon atom); (7) $\text{CH}_3/\text{olefin}$ is number of methyl groups per olefin molecule; (8) $\text{CH}_2/\text{olefin}$ is the number of methylene groups per olefin molecule; (9) $\text{C}_{\text{ave}}/\text{olefin}$ is the average number of carbon atoms per olefin molecule; (10) pour point was determined by the method of ASTM D-97; (11) viscosities were determined by method of ASTM D-445

[0088]

TABLE 6

Comparison of 1-octadecene and 9-octadecene		
Species	normal 1-octadecene	9-octadecene (Example 11)
B.P. (at 8 mmHg) ° C.	145	162
Melting Point, ° C.	17.5	-30.5
Refractive Index	1.4478	1.4470
(η_D , 20° C.)		
Density, g/cc	0.7891	0.7916

[0089] Table 7 below characterizes the composition of selected examples.

TABLE 7

Characterization of Examples 11, 13, 22, and 23	
Ex. No.	Characterization
11	The self-metathesis product of 1-decene using a rhenium comprising metathesis catalyst.
13	The product formed by isomerization of Example 11 (the metathesis product) using an Al_2O_3 isomerization catalyst.
22	A commercial synthetic olefin fluid intended for use as a major component of well fluid base oils available from BP Corporation sold under the trade name of Amodrill®.
23	A blend consisting of 15 weight percent of Example 11 and 85 weight percent of Amodrill® (Example 22).

[0090] Table 8 below lists some properties of for these selected examples, especially those properties that are significant in terms of use of these liquids in well fluid base oils.

TABLE 8

Properties of Examples 11, 13, 22, and 23				
Example Number	11	13	22	23
metathesis catalyst	Re	Re	N/A	Re
weight percent linear	99.4	97.7	70.6	75.0
pour point, ° C.	0	-18	-18	-21
viscosity 40° C., cSt	11,279	12,305	6,245	8,134

TABLE 8-continued

Properties of Examples 11, 13, 22, and 23					
Example Number	11	13	22	23	
Ref. Std. Toxicity, mg/kg	8136	5763	5743	5763	
Toxicity Ratio	0.63	0.43	0.78	0.62	
Toxicity PASS/FAIL	PASS	PASS	PASS	PASS	

[0091] In Table 8, viscosity at 40° C. was measured by the method of ASTM D-445 and pour point was measured by the method of ASTM D-97. As can be appreciated, all of the examples in Table 8 have outstanding toxicity characteristics. The pour point of Example 11 was 0° C. before isomerization but dropped to -18° C. after isomerization (Example 13). The isomerization process also caused the toxicity ratio to drop from 0.63 to 0.43. Obviously the process of this invention, metathesis followed by isomerization, produces liquids with extremely salient properties.

[0092] It can be seen from the data in Table 8 that the 9-octadecene produced by metathesis and isomerized 9-octadecene products have a unique combination of physical and environmental characteristics for use as well fluid base oils. The viscosity of these products is sufficiently low to be favored as well fluid base oils. The pour point of the 9-octadecene product and especially the isomerized 9-octadecene product are very useful in cold climates or offshore drilling conditions. The toxicity of the 9-octadecene, isomerized 9-octadecene, Amodrill®, and the mixture containing 15% of the 9-octadecene and 85% Amodrill® were measured using ASTM method E1367-99 test protocol as required in the U.S. EPA NPDES (National Pollution Discharge Elimination System) General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico. This protocol uses leptochierus plumulosus in a 10-day sediment toxicity test using a reference standard C1618 internal olefin having approximately 65% C16 and 35% C18 olefin. A passing result in this test protocol is indicated by a toxicity ratio value of the LC_{50} values less than 1.0 as calculated by Equation 1:

Toxicity Ratio =

Equation 1

$$\frac{10\text{-day } LC_{50}(\text{standard})}{10\text{-day } LC_{50} \text{ fluid} + (0.2 \times 10\text{-day } LC_{50}(\text{standard}))}$$

[0093] The data in Table 8 illustrate the significant reduction in toxicity of the 9-octadecene products compared with the reference standard. All of the metathesis products listed in Table 8 are significantly less toxic than the reference standard. A reduction in toxicity is also illustrated by a 15% metathesis product blend containing 85% Amodrill®. Data for Amodrill® are also listed in Table 8 to illustrate relative toxicity values for typical internal olefin products currently used as well fluid base oils in oil and gas well drilling applications.

Example 24

[0094] Example 24 was done to illustrate the cross-metathesis embodiment of the inventive process. For Example 24, 1-octene and 1-decene were subjected to cross-metathesis in a manner similar to previous examples of self-metathesis of 1-decene. Experimental conditions were: 10 grams of catalyst A in a tubular fixed bed reactor with upflow of the continuous liquid feed, feed was 30 wt % 1-octene and 70 wt % 1-decene, 1.0 WHSV (weight hourly space velocity), co-current nitrogen purging using 1.5 g N₂ per g of liquid feed, and a metathesis reactor temperature of 40° C. The reactor product sample was taken after 24 hours of reaction time. The resulting compositions are given in Table 9 below.

TABLE 9

Cross Metathesis of 1-octene and 1-decene		
Species	Feed, wt %	Product, wt %
light gases	0	10
C2 to C7 olefins		
C8 olefins	30	2.9
C10 olefins	70	6.5
C11 olefins	0	0.3
C12 olefins	0	0.1
C13 olefins	0	0.3
C14 olefins	0	7.9
C15 olefins	0	2.5
C16 olefins	0	32.9
C17 olefins	0	1.8
C18 olefins	0	34.8
Totals	100	100

[0095] Conversion of 1-octene and 1-decene was 90% and 91%, respectively. The product contains light gases and olefins other than the desired C₁₄ to C₁₈ olefins. These unwanted olefins are present in minor quantities and probably as a result of ethenolysis, and unwanted metathesis and cross-metathesis. The selectivity to the desired C₁₄ to C₁₈ range olefins was an outstanding 88%.

[0096] Reasonable variation and modification are possible in the scope of the foregoing disclosure, the examples, and the appended claims to this invention, the essence of which is that valuable liquid products are formed by mild metathe-

sis of linear alpha-olefins of carbon count C₄ to C₂₂. Well fluid base oils comprising these liquids are non-toxic to marine life and have low temperature pour points in the range of about 0° C. Subjecting these liquids to isomerization conditions in the presence of an isomerization catalyst further enhances the properties of well fluid base oil comprising them in that the pour point temperatures are decreased an additional 15° C. to 40° C. and the toxicity characteristics are also improved.

We claim:

1. A process for production of valuable liquid products suitable for use as at least one component in low pour point temperature and low toxicity well fluid base oils comprising the steps of:

- (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,
- (ii) subjecting said feed to metathesis conditions in the presence of a metathesis catalyst so as to form valuable liquid metathesis products and gaseous ethylene as a by-product,
- (iii) separating the valuable liquid metathesis products from the gaseous ethylene so as to drive the reaction to completion and permit recovery of the valuable liquid metathesis products,
- (iv) optionally, further purifying the liquid metathesis products from step (iii), and
- (v) subjecting a feed comprising about 10 to 100 weight percent of the product selected from step (iii), step (iv) and mixtures thereof to isomerization conditions in the presence of an isomerization catalyst.

2. The process of claim 1 wherein the metathesis catalyst comprises rhenium.

3. The process of claim 1 wherein the metathesis temperature is in the range of about 10° C. to about 150° C.

4. The process of claim 1 wherein the gaseous ethylene by-product is removed by deployment of an inert gas purge of the metathesis reactor during the linear alpha-olefin metathesis

5. The product made by the process of claim 1.

6. A well fluid base oil comprising the product of claim 5.

7. A process for production of valuable liquid products suitable for use as at least one component in low pour point temperature and low toxicity well fluid base oils comprising the steps of:

- (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,
- (ii) subjecting said feed to metathesis conditions in the presence of a heterogeneous supported metathesis catalyst so as to form valuable liquid metathesis products and gaseous ethylene as a by-product,
- (iii) separating the valuable liquid metathesis products from the gaseous ethylene so as to drive the reaction to completion and permit recovery of the valuable liquid metathesis products,
- (iv) optionally, further purifying the liquid metathesis products from step (iii), and

- (v) optionally, subjecting a feed comprising about 10 to 100 weight percent of the product selected from step (iii), step (iv) and mixtures thereof to isomerization conditions in the presence of an isomerization catalyst.
8. The process of claim 7 wherein the metathesis catalyst comprises rhenium.
9. The process of claim 7 wherein the metathesis temperature is in the range of about 10° C. to about 150° C.
10. The process of claim 7 wherein the gaseous ethylene by-product is removed by deployment of an inert gas purge of the metathesis reactor during the linear alpha-olefin metathesis.
11. The product made by the process of claim 7.
12. A well fluid base oil comprising the product of claim 7.
13. A process for production of specialty linear internal olefins comprising the steps of:
- (i) providing a predominantly linear alpha-olefins feed wherein said alpha-olefins have from about 4 to about 22 carbon atoms,
 - (ii) subjecting said feed to metathesis conditions in the presence of a heterogeneous supported metathesis catalyst so as to form valuable liquid specialty linear internal olefins and gaseous ethylene as a by-product,
 - (iii) separating the valuable liquid specialty internal olefin products from the gaseous ethylene so as to drive the reaction to completion and recover the valuable liquid specialty internal olefin products, and
 - (iv) optionally, further purifying the liquid specialty internal olefins metathesis products from step (iii).
14. The process of claim 13 wherein the metathesis catalyst comprises rhenium.
15. The process of claim 13 wherein the metathesis temperature is in the range of about 10° C. to about 150° C.
16. The process of claim 13 wherein the gaseous ethylene by-product is removed by deployment of an inert gas purge of the metathesis reactor during the linear alpha-olefin metathesis
17. The product made by the process of claim 13.
18. A well fluid base oil comprising the product of claim 17.
19. A lube oil additive comprising the product of claim 17.
20. A lube oil comprising the product of claim 17.
21. A lube oil comprising the hydrogenated product of claim 17.
22. A metal working lubricant comprising the product of claim 17.
23. A metal working lubricant comprising the hydrogenated product of claim 17.
24. A component of a metal working fluid comprising the product of claim 17.
25. A surfactant comprising product formed by chemically adding a polar group to the product of claim 17.
26. An alkenyl succinic anhydride compound formed by chemically reacting maleic anhydride with a feed comprising the product of claim 17.
27. A plasticizer comprising the product of claim 17.
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