

MANUFACTURING HYDROCARBON FLUIDS

FIELD

[0001] The techniques described herein provide systems and methods for manufacturing a hydrocarbon fluids from a light hydrocarbon stream. The light hydrocarbon stream is processed in to generate a mixture of compounds that are oligomerized and hydro-processed to form the hydrocarbon fluids.

BACKGROUND

[0002] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present techniques. This description is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0003] High molecular weight paraffins suitable for the production of high quality hydrocarbon fluids and distillate fuel may be in short supply or expensive to manufacture. In addition, the oligomerization of olefins is typically performed with high purity feed streams, such as polymer grade ethylene. For example, the production of hydrocarbon fluids from light hydrocarbon streams may involve numerous steps, which affect the costs for the final products. One example of the production of these compounds is the production of syngas, CO and H₂ by reforming, followed by Fischer-Tropsch reactions which preferentially synthesize linear high molecular weight products.

[0004] Some previous research activities have focused on using impure ethylene feeds to produce polyalphaolefins (PAOs). For example, U.S. Patent Application Publication No. 2010/0249474 by Nicholas et al. discloses a “process for oligomerizing dilute ethylene.” As described in the publication, a fluid catalytic process (FCC) may provide a dilute ethylene stream, as heavier hydrocarbons are processed. The ethylene in the dilute ethylene stream may be oligomerized using a catalyst, such as an amorphous silica-alumina base with a Group VIII or VIB metal that is resistant to feed impurities such as hydrogen sulfide, carbon oxides, hydrogen and ammonia. About 40 wt. %, or greater, of the ethylene in the dilute ethylene stream can be converted to heavier hydrocarbons.

[0005] Further, U.S. Patent Application Publication No. 2014/0275669 by Daage et al. discloses the “production of lubricant base oils from dilute ethylene feeds.” As described in this publication, a dilute ethylene feed, for example, formed while cracking heavier hydrocarbons, may be oligomerized to form oligomers for use as fuels or lubricant base oils. The

oligomerization of the impure dilute ethylene is performed with a zeolitic catalyst. The zeolitic catalyst is resistant to the presence of poisons such as sulfur and nitrogen in the ethylene feed. Diluents such as light paraffins, may be present without interfering with the process.

[0006] The feed used for both processes described above may be derived from the processing of oil in a fluid catalytic cracker (FCC). In an FCC, heavier hydrocarbons, such as crude oil fractions with a molecular weight of about 200 to about 600, or higher, are contacted with a catalyst at high temperatures to form lower molecular weight compounds. The byproduct gases from the FCC include olefins that may be used to form the oligomers.

SUMMARY

[0007] In an embodiment, the present invention provides a system for manufacturing a base stock from a light hydrocarbon stream. The system includes a cracker configured to form a raw product stream from the light hydrocarbon stream, a separator configured to remove water from the raw product stream forming an oligomerization feed stream, and an oligomerization reactor configured to increase a molecular weight of the oligomerization feed stream forming a raw oligomer stream. The system further includes a distillation column configured to separate a heavy olefinic stream from the raw oligomer stream and a hydro-processing reactor configured to hydro-process the heavy olefinic stream to form a hydro-processed stream. A product distillation column is configured to separate the hydro-processed stream to form the base stock.

[0008] In another embodiment, the present invention discloses a method for manufacturing a base stock from a light hydrocarbon stream. The method includes cracking the light hydrocarbon stream to form a raw product stream, removing water from the raw product stream to form an oligomerization feed stream, and oligomerizing the oligomerization feed stream to form an intermediate stream. A heavy olefinic stream is distilled from the intermediate stream, and the heavy olefinic stream is hydro-processed to form a hydro-processed stream. The hydro-processed stream is distilled to form the base stock.

[0009] In another embodiment, the present invention provides a system for manufacturing a base oil stock from a light hydrocarbon stream. The system includes a steam cracker to form a raw product stream from the light hydrocarbon stream. A separator is configured to remove naphtha, water, steam cracker gas oil (SCGO), and tar from the raw product stream to form an oligomerization feed stream. An oligomerization reactor is configured to convert the oligomerization feed stream to a higher molecular weight stream by contacting the oligomerization feed stream with a heterogeneous catalyst. A distillation column is configured to separate a heavy olefinic stream from the higher molecular weight stream. The distillation

column is configured to recover a light alpha-olefin stream from the higher molecular weight stream. A hydro-processing reactor is configured to demetallate the heavy olefinic stream, to crack the heavy olefinic stream, to form isomers in the heavy olefinic stream, or to hydrogenate olefinic bonds in the heavy olefinic stream, or any combinations thereof. A product distillation column is configured to separate the isomers in the heavy olefinic stream to form a plurality of base stock streams.

DESCRIPTION OF THE DRAWINGS

[0010] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings.

[0011] **Fig. 1** is a simplified block diagram of a system for producing hydrocarbon fluids from a light gas feed, in accordance with examples.

[0012] **Fig. 2** is a process flow diagram of a method for producing hydrocarbon fluids from a light hydrocarbon stream, in accordance with examples.

[0013] **Fig. 3** is a plot of the yield of different weight molecules, showing the changes as the catalyst is changed, in accordance with examples.

[0014] **Fig. 4** is a plot of a simulated distillation by gas chromatography comparing the products for a gas feed with hydrogen to a gas feed without hydrogen, in accordance with examples.

[0015] **Figs. 5(A) and 5(B)** are plots of C-13 NMR spectra comparing a test product to a hydrocarbon fluid.

[0016] **Figs. 6(A) to 6(C)** are 1-H NMR spectra comparing test products to a Group II hydrocarbon base stock.

DETAILED DESCRIPTION

[0017] In the following detailed description section, specific embodiments of the present techniques are described. However, to the extent that the following description is specific to a particular embodiment or a particular use of the present techniques, this is intended to be for exemplary purposes only and simply provides a description of the exemplary embodiments. Accordingly, the techniques are not limited to the specific examples described below, but rather, include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

[0018] Recent improvements in the production of hydrocarbons, for example, the use of hydraulic fracturing and tertiary oil recovery techniques, have resulted in the increased availability of lower molecular weight hydrocarbons, termed light hydrocarbon streams herein.

These include natural gas and natural gas liquids (NGL), which may include methane, ethane, propane, and butane, along with other hydrocarbon and heteroatom contaminants. The use of the lower molecular weight hydrocarbons as feedstocks for chemical processes may provide economic benefits. However, upgrading the lower molecular weight feedstocks to increase the molecular weight may pose challenges.

[0019] The techniques described herein disclose a method for producing high molecular weight molecules from a raw olefin stream that may include olefins, paraffins, hydrogen, and carbon monoxide. The raw olefin stream is provided by a steam cracking reactor, or cracker, which may be controlled to provide a higher molecular weight feed stock from a light hydrocarbon stream. The light hydrocarbon stream has an API gravity of at least 45, at least 50, at least 55, at least 60, at least 65, or at least 70 according to various embodiments of the present invention. Further, the hydrogen content of the starting raw hydrocarbons may be greater than or equal to 14 %, or, in some examples, greater or equal to 16 %. In some examples, the light hydrocarbon stream may also include compounds having two to four, two to six, two to 12, or two to 20, or more, carbon atoms. In some examples, the feed is a natural gas liquids (NGL) stream. In other examples, the feed includes methane, ethane, propane, or butane. In some examples, the light hydrocarbon feedstock has an API gravity of between about 45 and 55 and includes molecules with carbon chains of about two to 25 carbon atoms in length, among others. In other examples, the light hydrocarbon feedstock has an API gravity of between about 55 and 65 and includes molecules with about two to 10 carbon atoms, among others. In other examples, the light hydrocarbon feedstock has an API gravity of between about 55 and 65 and includes molecules with about two to 10 carbon atoms, among others. In yet other examples, the light hydrocarbon feedstock has an API gravity of between about 65 and 75 and includes molecules with about two to five carbon atoms, among others.

[0020] The light hydrocarbon stream may be sourced from any number of hydrocarbon formations, including, for example, tight gas formations. These may include the Clinton, Medina, and Tuscarora formations in Appalachia, the Berea sandstone in Michigan, the Bossier, Cotton Valley, Olmos, Vicksburg, and Wilcox Lobo formations along the Gulf Coast, the Granite Wash and Atoka formations in the Midcontinent, the Canyon formation and other formations, in the Permian Basin, and the Mesaverde and Niobrara formations in multiple Rocky Mountain basins. Any number of other formations may be used to provide the light hydrocarbon stream, such as the Rotliegend Group of formations in Germany and the Netherlands, the Eagle Ford group in Texas, and the Bakken formations in Montana, North Dakota, Saskatchewan, and Manitoba.

[0021] As used herein “cracking” is a process that uses decomposition and molecular recombination of organic compounds to produce a greater number of molecules than were initially present. In cracking, a series of reactions take place accompanied by a transfer of hydrogen atoms between molecules. Cracking may be performed in a thermal cracking process, a steam cracking process, a catalytic cracking process, or a hydrocracking process, among others. For example, naphtha, a hydrocarbon mixture that is generally a liquid having molecules with about five to about twelve carbon atoms, may undergo a thermal cracking reaction to form ethylene and H₂ among other molecules. In some examples, the free radicals formed during the cracking process may form compounds that are more complex than those in the feed.

[0022] A separation train after a steam cracker may include over a dozen steps and pieces of equipment to produce high purity polymer grade ethylene. In addition, the raw product stream may be compressed from about 10 psig to about 550 psig before entering a cold box to remove H₂, CO, and CH₄ impurities. Decreasing the process pressure greatly reduces the cost of separation and thus the overall process. An exemplary simple separation may include a primary fractionator, a caustic tower, a drier, and an acetylene converter. Further, the raw product stream may be compressed to only about 250 psig to implement the simple separation, lowering costs over compression to 550 psig. The elimination of the remaining back-end separation train decreases the cost of production, but produces an impure olefin stream that can be processed by the impure olefin stream conversion process to produce higher molecular weight products.

[0023] To avoid the need for separation, the techniques use poison tolerant heterogeneous catalysts, such as zeolites, that are capable of olefin oligomerization in the presence of hydrogen and carbon monoxide. The products include hydrocarbon fluids, such as gasoline, diesel, and lubricant range linear and isoparaffins, in addition to highly branched molecules useful for chemical applications, such as base stocks.

[0024] As used herein, “hydrocarbon fluids” refers to isoparaffinic hydrocarbons in a naphtha and distillate range of molecular weights. Lightly or highly branched paraffinic molecules are useful as hydrocarbon fluids or transportation fuels. Hydrocarbon fluids may include hydrocarbon fluids used for forming lubricants. As used herein, “base stock” or “base oil stock” refers to hydrocarbons in a lubricant range of molecular weights. Lightly or highly branched molecules of lower molecular weights are useful as hydrocarbon fluids or transportation fuels. Group I hydrocarbon fluids or base oils are defined as base oils with less than 90 wt. % saturated molecules and/or at least 0.03 wt. % sulfur content. Group I hydrocarbon fluids also have a viscosity index (VI) of at least 80 but less than 120. Group II hydrocarbon fluids or base oils

contain at least 90 wt. % saturated molecules and less than 0.03 wt. % sulfur. Group II hydrocarbon fluids also have a viscosity index of at least 80 but less than 120. Group III hydrocarbon fluids or base oils contain at least 90 wt. % saturated molecules and less than 0.03 wt. % sulfur, with a viscosity index of at least 120.

[0025] Further, the hydrocarbon fluids may be referred to as light neutral (LN), medium neutral (MN), and heavy neutral (HN), for example, as determined by viscosity. The term “neutral” generally indicates the removal of most nitrogen and sulfur atoms to lower reactivity in the final oil. The hydrocarbon fluids are generally classified by viscosity, measured at 40 °C as a kinematic viscosity under the techniques described in ASTM D445. The viscosity may be reported in millimeters²/second (centistokes, cSt). The hydrocarbon fluids may also be classified by boiling point range, for example, determined by simulated distillation on a gas chromatograph, under the techniques described in ASTM D 2887. It should be noted that the viscosity ranges and boiling point ranges described herein are merely examples, and may change, depending on the content of linear paraffins, branched paraffins, cyclic hydrocarbons, and the like. A light neutral base stock may have a kinematic viscosity of about 4 cSt to about 6 cSt and may have a boiling point range of about 380 °C to about 450 °C. A medium neutral base stock may have a kinematic viscosity of about 6 cSt to about 10 cSt and a boiling point range of about 440 °C to about 480 °C. A heavy neutral base stock may have a kinematic viscosity of about 10 cSt to about 20 cSt, or higher, and a boiling point range of about 450 °C to about 565 °C.

[0026] As used herein, a “catalyst” is a material that increases the rate of specific chemical reactions under certain conditions of temperature and pressure. Catalysts may be heterogeneous, homogenous, and supported. A heterogeneous catalyst is a catalyst that has a different phase from the reactants. The phase difference may be in the form of a solid catalyst with liquid or gaseous reactants or in the form of immiscible phases, such as an aqueous acidic catalyst suspended in droplets in an organic phase holding the reactants. A heterogeneous catalyst may be bound, such as a zeolite bound with alumina or another metal oxide. A homogeneous catalyst is soluble in the same phase as the reactants, such as an organometallic catalyst dissolved in an organic solvent with a reactant.

[0027] In an example of a process to convert light gas to high quality hydrocarbons and base oil stocks, for example, using the system and method of **Figs. 1 and 2**, a light hydrocarbon stream, that may include ethane, is converted, via steam cracking, to an impure olefinic stream or raw product stream. The raw product stream is then sent to a quench fractionator where naphtha, water, steam cracking gas oil, and tar are separated out to form an oligomerization feed stream.

The oligomerization feed stream may contain ethylene, propylene, acetylene, propyne, hydrogen, carbon monoxide, methane, ethane, propane, hydrogen disulfide, carbon monoxide, and water. Additional impurities in the ppb level such as Hg, PH₃, AsH₃, COS, and NO_x may also be contained in the stream.

[0028] The oligomerization feed stream may be processed by a caustic tower to remove H₂S and CO₂ as well as a drier to remove excess water. As used herein, a “caustic tower” is a separation tower in which a caustic solution, such as an aqueous solution of sodium hydroxide, is contacted with a hydrocarbon stream to remove some heteroatom impurities, such as sulfur compounds and carbon dioxide. The caustic tower may use any number of internal flow arrangements, such as co-current flows and counter-current flows, among others. Other units, such as settlers, may be used with the caustic tower to separate the hydrocarbon from the caustic solution.

[0029] The oligomerization feed stream then enters the oligomerization process, which converts the olefins in the oligomerization feed stream to higher molecular weight products. The conversion may be performed in a number of different reactor types including but not limited to a fixed bed, a slurry-bubble column, a CSTR, or a moving bed. As described herein, a heterogeneous catalyst may be used, for example, taking the form of extrudates or small spheres or particles. The space velocity over the catalyst could range from about 0.05 to about 50 WHSV depending on the desired product composition. The higher molecular weight products containing gasoline, diesel, and base stock can be separated. These materials may be used as is, or may be hydro-processed, as described herein. For example, they may be hydrotreated to remove heteroatoms and saturate olefins. The process conditions and catalyst for the hydro-processing of paraffins and isoparaffins are known in the art.

[0030] For ease of reference, certain terms used in this application and their meanings as used herein are set forth. To the extent a term is not defined herein, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Further, the present techniques are not limited by the usage of the terms shown herein, as all equivalents, synonyms, new developments, and terms or techniques that serve the same or a similar purpose are considered to be within the scope of the present claims.

[0031] **Fig. 1** is a simplified block diagram of a system **100** for producing hydrocarbon fluids from a light gas feed, in accordance with examples. The process begins with the introduction of a hydrocarbon feed stream, such as a light hydrocarbon stream **102**, to a steam cracker **104**. As

used herein, a hydrocarbon feed stream may include a composition prior to any treatment, such treatment including cleaning, dehydration or scrubbing, as well as any composition having been partly, substantially or wholly treated for the reduction or removal of one or more compounds or substances, including, but not limited to, sulphur, sulphur compounds, carbon dioxide, water, mercury, and one or more C₂+ hydrocarbons, such as ethane, propane, butane, and the like.

Steam Cracking

[0032] In the steam cracker **104**, the light hydrocarbon stream **104** is diluted with steam, and then briefly heated to high temperatures in a steam cracker, such as above 800 °C, before the reaction is quenched. The reaction time may be milliseconds in length. Oxygen is excluded to prevent degradation and decrease the formation of carbon oxides. The mixture of products in the raw product stream **106** from the steam cracker **104** may be controlled by the feedstock, with the lighter feedstocks of the light hydrocarbon stream **102**, such as ethane, propane, or butane, or combinations thereof, among others, favoring the formation of lighter products, such as ethylene, propylene, or butadiene, among others. The product distribution in the raw product stream **106** may also be controlled by the steam/hydrocarbon ratio, the reaction temperature, and the reaction time, among other factors.

[0033] A separator **108** may be used to separate the water formed from the steam and degradation products, from the raw product stream **106** to form an oligomerization feed stream **110**. The separator **108** may include a flash tank to allow water to condense and settle, while product gases flow out, forming the oligomerization feed stream **110**. In some examples, chiller systems may be used to condense the water from the raw product stream **106**.

[0034] After water removal, the oligomerization feed stream **110** may include, for example, approximately 5 % to 90 % olefin (ethylene, propylene, butylene, and the like), 5 % to 80 % hydrogen, 0 to 20 % alkyne (acetylene, propyne, and the like), 0 % to 50 % paraffin (methane, ethane, C₃+), 10 to 10,000 wt. ppm of carbon monoxide, and trace water. In some examples, the oligomerization feed stream **110** includes 35 % to 55 % olefin, 30 % to 60 % hydrogen, 0.5 % to 3 % alkyne, 5 % to 30 % paraffin, and 500 to 2,000 wt. ppm of carbon monoxide.

Oligomerization

[0035] The oligomerization feed stream **110** is provided to an oligomerization reactor **112**, where it is contacted with a zeolite catalyst **114**. The zeolite catalyst **114** is generally a poison tolerant and regenerable catalytic zeolite capable of the oligomerization of impure and dilute olefins to C₁₀+ products or C₂₅+ to produce diesel, lube, and hydrocarbon fluid molecules. The zeolites suitable for this conversion include, but are not limited to, 10-ring zeolites such as

ZSM-5 (MFI), ZSM-11 (MEL), ZSM-48 (MRE), and the like, with Si/Al₂ ratios from 5 to 500. The zeolites are used in their proton form and may or may not be promoted with metals by ion exchange or impregnation. In addition, the binder used during formulation be used to control the yield and product slate.

[0036] The oligomerization process can be performed as a single step process or a two-step process. In a single step process, the oligomerization reactor **112** performs the oligomerization in a single stage or in a single reactor in. The oligomerization feed stream **110** is introduced into the single stage as a gas phase feed. The oligomerization feed stream **110** is contacted with the zeolite catalyst **114** under effective oligomerization conditions. For example, the ethylene feed can be contacted with the zeolite catalyst at a temperature of 20 °C to 300 °C, such as at least 25 °C or at least 50 °C or at least 100 °C and 250 °C or less, or 225 °C or less. The ethylene feed can be contacted with the catalyst at a gas hourly space velocity, based on ethylene, of 1 hr⁻¹ to 500 hr⁻¹, such as at least 5 hr⁻¹ or at least 10 hr⁻¹ or at least 20 hr⁻¹ or at least 30 hr⁻¹ and 250 hr⁻¹ or less or 100 hr⁻¹ or less. The total pressure can be from 1 atm (100 kPa) to 200 atm (20.2 MPa), and about 100 atm (10.1 MPa) or less. Optionally, the oligomerization feed is contacted with the catalyst at a hydrogen partial pressure that is at least 1 % of the total pressure, such as at least 5 % of the total pressure at least 10 % of the total pressure, or up to 50 % of the total feed on a volumetric basis. The reaction forms a raw oligomer stream **116** that can then be fractionated in a distillation column **118**.

[0037] In a two-step process, a first oligomerization to C₆+ olefins, for example, C₆ and higher carbon number oligomers, is achieved under gas phase conditions similar to those described above. The product is then condensed to recover the C₆+ olefins or to recover C₁₀+ olefins, such as C₁₀ and higher carbon number oligomers. Recovering the C₆+ olefins roughly corresponds to recovering an intermediate portion from the first oligomerization having a boiling point of 60 °C or greater. Recovering the C₁₀+ olefins roughly corresponds to recovering an intermediate portion with a boiling point of at least 170 °C.

[0038] Accordingly, the intermediate product that is recovered for further oligomerization can correspond to an intermediate product with an initial boiling point of at least 60 °C, such as at least 100 °C, or at least 150 °C. The resulting intermediate product is then further oligomerized in presence of an acid catalyst under liquid phase conditions to produce higher molecular weight molecules, such as with more than 20 carbons atoms (C₂₀+), or with more than 26 carbon atoms (C₂₆ +). For the liquid phase oligomerization, the olefin-containing feed from the first stage can be contacted with the catalyst at a temperature from 20 °C to 300 °C, such as at least 25 °C, or at

least 50 °C, or at least 100 °C, 250 °C or less, or 225 °C or less. The total pressure can be from 1 atm

(100 kPag) to 200 atm (20.2 MPag), or 100 atm (10.1 MPag) or less. In some examples, the liquid oligomerization feed can be contacted with the catalyst at a hydrogen partial pressure that is at least 1 % of the total pressure, such as at least 5 % of the total pressure or at least 10 % of the total pressure.

[0039] The oligomerization reactor **112** may use a recycle loop to allow lower molecular weight oligomers to be recycled to the cracker **104**, or to be provided to other reaction systems, such as a dimerization or alkylation unit, to increase the yield of products. For example, in a single step oligomerization process, the oligomers formed during oligomerization may be roughly divided into three types of compounds. A first type of compounds, termed a light olefinic stream **120**, corresponds to compounds having about 10 carbon atoms or less. Such compounds correspond to naphtha boiling range compounds. Due to the lower value of naphtha relative to lubricant base oils, a portion of the naphtha boiling range compounds can optionally be recycled to the steam cracker **104** in order to increase the yield of the oligomerization feed stream **110**. This can allow the naphtha boiling range compounds to be recycled and converted into higher value products. In some examples, lower molecular weight linear alpha-olefins, e.g., with less than about 10 carbon atoms, may be recovered from the light olefinic stream **120** as a product stream, for example, for polymerization processes.

[0040] A second group of compounds, termed an intermediate olefinic stream **122**, may have between about 10 and about 25 carbon atoms. These compounds may correspond to distillate fuel compounds, such as diesel or kerosene, and include other olefinic compounds. As for the light olefinic stream **120**, the intermediate olefinic stream **122** may be partially, or fully, recycled to the cracker **104** to increase the yield of the oligomerization feed stream **110**. Further, the intermediate olefinic stream **122** may be used as a feedstock for other processes, such as dimerization or alkylation. In some examples, the intermediate olefinic stream **122** may be combined into other streams prior to final product separation, as described herein.

[0041] The third group of compounds, termed a heavy olefinic stream **124**, may have at least about 24 carbon atoms. It may be noted that the olefinic streams **120**, **122**, and **124** may not be composed of 100 % olefinic compounds, but may include a number of other compounds, such as paraffin, that are removed in the same boiling point ranges as the olefinic compounds. For example, the light olefinic stream **120** may include, for example, linear alpha-olefins having from about four carbon atoms to about 10 carbon atoms and unreacted ethylene. Further, as higher

molecular weight compounds are formed, the amounts of paraffinic compounds may increase as well. These compounds may correspond to lubricant boiling range compounds. To lower the amounts of contaminants, as well as to upgrade the final products, the heavy olefinic stream **124** may be provided to a hydro-processing reactor **126**. It may be noted that the olefinic streams **120**, **122**, and **124** may not be pure olefins, but may include other compounds with similar boiling points, such as paraffinic compounds. The paraffin content often increases with the molecular weight.

[0042] Various types of hydro-processing can be used in the production of hydrocarbon fluids, such as fuels, naphtha's, and base stocks. For example, a catalytic dewaxing, or hydrocracking/hydroisomerization (HDC/HDI) process, may be included to modify viscosity properties or cold flow properties, such as pour point and cloud point. The hydrocracked or dewaxed feed can then be hydrofinished, for example, to saturate olefins and aromatics from the olefinic streams **120**, **122**, and **124**.

Hydro-Processing

[0043] As used herein, "hydro-processing" includes any hydrocarbon processing that is performed in the presence of hydrogen, such as hydroconversion, hydrocracking, hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, and hydroisomerization, among others. The hydrogen may be added to the hydro-processing reactor **126** as a hydrogen treat stream **128**. The hydrogen may be added to the hydro-processing reactor **126** as one or more hydrogen treat streams **128**. The products of the hydro-processing reactor **126**, termed a hydro-processed stream **130**, may have lower contaminants, including metals and heteroatom compounds, as well as improved viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization, and the like.

[0044] The products of the hydro-processing reactor **126**, termed a hydro-processed stream **130**, may have lower contaminants, including metals and heteroatom compounds, as well as improved viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization, and the like.

[0045] After forming compounds by oligomerization, and separating out the light olefinic stream **120** and the intermediate olefinic stream **122**, the heavy olefinic stream **124** may be provided to the hydro-processing reactor **126** to remove contaminants and improve product properties, such as cold flow properties. In an example, the intermediate olefinic stream **122** may be blended with the heavy olefinic stream **124** and sent to the hydro-processing reactor **126**. For example, hydrotreatment or mild hydrocracking can be used for removal of

contaminants, and optionally to provide some viscosity index uplift, while hydroisomerization and hydrocracking, termed catalytic HDC/HDI, may be used to improve cold flow properties.

[0046] In the discussion below, a stage in a hydro-processing reactor **126** can correspond to a single reactor or a plurality of reactors. In some examples, multiple reactors can be used to perform one or more of the processes, or multiple parallel reactors can be used for all processes in a stage. Each stage or reactor may include one or more catalyst beds containing hydro-processing catalyst. Note that a catalyst bed in the discussion below may refer to a partial physical catalyst bed. For example, a catalyst bed within a reactor could be filled partially with a hydrocracking catalyst and partially with an HDC/HDI catalyst. For convenience in description, even though the two catalysts may be stacked together in a single catalyst bed, the hydrocracking catalyst and the HDC/HDI catalyst can each be referred to conceptually as separate catalyst beds.

[0047] In the discussion herein, the hydro-processing reactor **126** may include the one or more stages, such as two stages or reactors and an optional intermediate separator, that are used to contact a feed with a number of catalysts under hydro-processing conditions. The catalysts can be distributed between the stages or reactors in any convenient manner. The hydrogen treat stream **128** may be added to each of the stages or reactors separately, or may be added in fewer additions, such as to each reactor, or only a first reactor.

[0048] Various types of hydro-processing can be used in the production of fuels and/or lubricant base oils. Typical processes include a catalytic dewaxing, or hydrocracking/hydroisomerization (HDC/HDI) process, to modify viscosity properties or cold flow properties, such as pour point and cloud point. The hydrocracked or dewaxed feed can then be hydrofinished, for example, to saturate olefins and aromatics from the hydro-processed stream **130**. In addition to the above, a hydrotreatment stage can also be used for contaminant removal. The hydrotreatment of the oligomer feed to remove contaminants may be performed prior to or after the hydrocracking or the HDC/HDI.

Hydroisomerization / Hydrocracking (HDC/HDI)

[0049] Suitable HDC/HDI (dewaxing) catalysts may include molecular sieves such as crystalline aluminosilicates, or zeolites. In an example, the molecular sieve may be ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, or zeolite Beta, or may be any combinations thereof, such as ZSM-23 and ZSM-48, or ZSM-48 and zeolite Beta. Molecular sieves that are selective for dewaxing by isomerization, as opposed to cracking, may be used, such as ZSM-

48, zeolite Beta, ZSM-23, or any combinations thereof. The molecular sieves may include a 10-member ring 1-D molecular sieve. Examples include EU-1, ZSM-35 (or ferrierite), ZSM-11, ZSM-57, NU-87, SAPO-11, ZSM-48, ZSM-23, and ZSM-22. Some of these materials may be more efficient, such as EU-2, EU-11, ZBM-30, ZSM-48, or ZSM-23. Note that a zeolite having the ZSM-23 structure with a silica to alumina ratio of from 20:1 to 40:1 may be referred to as SSZ-32. Other molecular sieves that are isostructural with the above materials include Theta-I, NU-10, EU-13, KZ-1, and NU-23. The HDC/HDI catalyst may include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof, for example alumina and titania or silica and zirconia, titania, or both.

[0050] In various examples, the catalysts according to the disclosure further include a hydrogenation catalyst to saturate multiple bonds and aromatics, which may be termed hydrofinishing herein. The hydrogenation catalyst typically includes a metal hydrogenation component that is a Group VI and/or a Group VIII metal. In some examples, the metal hydrogenation component is a Group VIII noble metal. For example, the metal hydrogenation component may be Pt, Pd, or a mixture thereof. Further, the metal hydrogenation component may be a combination of a non-noble Group VIII metal with a Group VI metal. Suitable combinations can include Ni, Co, or Fe with Mo or W, or, in some examples, Ni with Mo or W.

[0051] The metal hydrogenation component may be added to the catalyst in any convenient manner. For example, the metal hydrogenation component may be combined with the catalyst using an incipient wetness. In this technique, after combining a zeolite and a binder, the combined zeolite and binder can be extruded into catalyst particles. These catalyst particles may then be exposed to a solution containing a suitable metal precursor. In some examples, metal can be added to the catalyst by ion exchange, where a metal precursor is added to a mixture of zeolite (or zeolite and binder) prior to extrusion.

[0052] The amount of metal in the catalyst may be at least about 0.1 wt. % based on catalyst, or at least about 0.15 wt. %, or at least about 0.2 wt. %, or at least about 0.25 wt. %, or at least about 0.3 wt. %, or at least about 0.5 wt. % based on catalyst. The amount of metal in the catalyst may be about 20 wt. % or less based on catalyst, or about 10 wt. % or less, or about 5 wt. % or less, or about 2.5 wt. % or less, or about 1 wt. % or less. For examples where the metal is Pt, Pd, another Group VIII noble metal, or a combination thereof, the amount of metal may be from about 0.1 to about 5 wt. %, about 0.1 to about 2 wt. %, or about 0.25 to about 1.8 wt. %, or about

0.4 to about 1.5 wt. %. For examples where the metal is a combination of a non-noble Group VIII metal with a Group VI metal, the combined amount of metal may be from about 0.5 wt. % to about 20 wt. %, or about 1 wt. % to about 15 wt. %, or about 2.5 wt. % to about 10 wt. %.

[0053] A zeolite can be combined with binder in any convenient manner. For example, a bound catalyst can be produced by starting with powders of both the zeolite and binder, combining and mulling the powders with added water to form a mixture, and then extruding the mixture to produce a bound catalyst of a desired size. Extrusion aids can also be used to modify the extrusion flow properties of the zeolite and binder mixture.

[0054] Process conditions in a catalytic HDC/HDI zone in a may include a temperature of from about 200 to about 450 °C, or from about 270 to about 400 °C, a hydrogen partial pressure of from about 1.8 MPag to about 34.6 MPag (about 250 psig to about 5000 psig), or from about 4.8 MPag to about 20.8 MPag, and a hydrogen circulation rate of from about 35.6 m³/m³ (200 SCF/B) to about 1781 m³/m³ (10,000 SCF/B), or from about 178 m³/m³ (1000 SCF/B) to about 890.6 m³/m³ (5000 SCF/B). In other examples, the conditions can include temperatures in the range of about 600 °F (343 °C) to about 815 °F (435 °C), hydrogen partial pressures of from about 500 psig to about 3000 psig (3.5 MPag-20.9 MPag), and hydrogen treat gas rates of from about 213 m³/m³ to about 1068 m³/m³ (1200 SCF/B to 6000 SCF/B). These latter conditions may be suitable, for example, if the HDC/HDI stage is operating under sour conditions, e.g., in the presence of high concentrations of sulfur compounds.

[0055] The liquid hourly space velocity (LHSV) can vary depending on the ratio of hydrocracking catalyst used to hydroisomerization catalyst in the HDC/HDI catalyst. Relative to the combined amount of hydrocracking and hydroisomerization catalyst, the LHSV may be from about 0.2 h⁻¹ to about 10 h⁻¹, such as from about 0.5 h⁻¹ to about 5 h⁻¹ and/or from about 1 h⁻¹ to about 4 h⁻¹. Depending on the ratio of hydrocracking catalyst to hydroisomerization catalyst used, the LHSV relative to only the HDC/HDI catalyst can be from about 0.25 h⁻¹ to about 50 h⁻¹, such as from about 0.5 h⁻¹ to about 20 h⁻¹, or from about 1.0 h⁻¹ to about 4.0 h⁻¹.

Hydro-finishing and Aromatic Saturation Process

[0056] In some examples, a hydrofinishing stage, an aromatic saturation stage, or both may be used. These stages are termed finishing processes herein. Finishing processes may improve color and stability in a final product by lowering the amounts of unsaturated or oxygenated compounds in the final product streams. The finishing may be performed in the hydro-processing reactor **126** after the last hydrocracking or hydroisomerization stage. Further, the finishing may occur after fractionation of a hydro-processed stream **128** in a product distillation column **132**. If

finishing occurs after fractionation, the finishing may be performed on one or more portions of the fractionated product, such as being performed on the heavy neutral stream **134** from the product distillation column **132**. In some examples, the entire effluent from the last hydrocracking or HDC/HDI process can be finished prior to fractionation into individual product streams.

[0057] In some situations, the finishing processes, including hydrofinishing and aromatic saturation, may refer to a single process performed using the same catalyst. Alternatively, one type of catalyst or catalyst system can be provided to perform aromatic saturation, while a second catalyst or catalyst system can be used for hydrofinishing. Typically the finishing processes will be performed in a separate reactor from the HDC/HDI or hydrocracking processes to facilitate the use of a lower temperature for the finishing processes. However, an additional hydrofinishing reactor following a hydrocracking or HDC/HDI process, but prior to fractionation, may still be considered part of a second stage of a reaction system conceptually.

[0058] Finishing catalysts can include catalysts containing Group VI metals, Group VIII metals, and mixtures thereof. In an example, the metals may include a metal sulfide compound having a strong hydrogenation function. The finishing catalysts may include a Group VIII noble metal, such as Pt, Pd, or a combination thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt. % or greater based on the catalyst. The metals and metal compounds may be supported, for example, on a metal oxide. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, or, in some examples, alumina.

[0059] The catalysts for aromatic saturation may include at least one metal having relatively strong hydrogenation function on a porous support. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The support materials may also be modified, such as by halogenation or fluorination. The metal content of the catalyst may be as high as 20 wt. % for non-noble metals. In an example, a hydrofinishing catalyst is a crystalline material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica content. Examples include MCM-41, MCM-48 and MCM-50. If separate catalysts are used for aromatic saturation and hydrofinishing, an aromatic saturation catalyst can be selected based on activity or selectivity for aromatic saturation, while a hydrofinishing catalyst can be selected based on activity for improving product specifications, such as product color and polynuclear aromatic reduction.

[0060] Finishing conditions can include temperatures from about 125 °C to about 425 °C, or about 180 °C to about 280 °C, a hydrogen partial pressure from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), or about 1500 psig (10.3 MPa) to about 2500 psig (17.2 MPa), and an LHSV from about 0.1 hr⁻¹ to about 5 hr⁻¹ LHSV, or, in some examples, 0.5 hr⁻¹ to 1.5 hr⁻¹. Additionally, a hydrogen treat gas rate of from about 35.6 m³/m³ to about 1781 m³/m³ (200 SCF/B to 10,000 SCF/B) can be used.

Fractionation and Products

[0061] After hydro-processing, the hydro-processed oligomers in the hydro-processed stream **130** can be fractionated in the product distillation column **132**. Any number of fractions may be isolated, including, for example, a distillate stream **136** that may include naphtha, diesel, or a distillate fuel fraction, among others. Fractions that form hydrocarbon fluids for lubricants and other hydrocarbon products, may be isolated, including, for example, a light neutral stream **138**, and a medium neutral stream **140**, in addition to the heavy neutral stream **134**, as described herein.

[0062] A bottoms stream **142** may also be isolated. In some examples, the bottoms stream **142** may be returned to the hydro-processing reactor **126** for further processing. Further, the bottoms stream **142** may be returned to the cracker **104**, for example, by being blended with the light hydrocarbon stream **102**, increasing the yield of the raw product stream **106**.

[0063] To form product streams, such as diesel fluid, naphtha, and gasoline, the intermediate olefinic stream **122** may be combined with the distillate stream **136** to form a combined stream **144** and further processed. In some examples, the combined stream **144** is hydro-processed, then distilled to form the product streams. This may be performed in a product isomerization reactor **146**, for example, using the process described herein, to hydroisomerize the combined stream **144**, to hydrogenate the combine stream **144**, or to perform other hydro-processing reactions. The hydro-processed product stream **148** may be provided to a product distillation column **150** for the separation of hydrocarbon fluids, such as a diesel fuel stream **152**, a gasoline stream **154**, and a light hydrocarbon fluid stream **156**. In an example, the light hydrocarbon fluid stream **156** includes isomers of C5 to C7 compounds. An overhead stream **158** may include very light hydrocarbons or gases, such as propane and butane. A heavy product stream **160** may be returned to the product isomerization reactor **146**. In some examples, the heavy product stream **160**, the overhead stream **158**, or both, are returned to the steam cracking reactor **104**.

Method for Producing Hydrocarbon Fluids from Light Hydrocarbon Streams

[0064] **Fig. 2** is a process flow diagram of a method **200** for producing hydrocarbon fluids from a light hydrocarbon stream, in accordance with examples. The method **200** may be implemented using the equipment and conditions described with respect to **Fig. 1**. The method begins at block **202** when a light hydrocarbon is cracked to form a raw product stream. This may be performed by contacting the light hydrocarbon stream with steam and a heterogeneous catalyst. Naphtha, steam cracking gas oil (SCGO), or tar, among others, may be separated from the raw product stream, for example, in a quench tower. Further, hydrogen sulfide, carbon dioxide, or both, may be separated from the raw product stream, for example, using a caustic tower or an amine separator.

[0065] At block **204**, water is removed from the raw product stream to form an oligomerization feed stream. As described herein, this may be performed using a condenser, a cold box, a molecular sieve tower, and the like.

[0066] At block **206**, the oligomerization feed stream is oligomerized to form an intermediate stream. As described herein, this may be performed by contacting the oligomerization feed stream with a heterogeneous catalyst including a zeolite on a metal oxide support. The composition of the intermediate stream may be controlled by changing a ratio of the zeolite to the metal oxide support. A light olefinic stream may be distilled from the intermediate stream. Further, a heavy olefinic stream may be distilled from the intermediate stream.

[0067] At block **208**, a heavy olefinic stream is distilled from the intermediate stream. At block **210**, the heavy olefinic stream is hydro-processed to form a hydro-processed stream. In the hydro-processing, the heavy olefinic stream may be hydrocracked to form lower molecular weight compounds, for example, having a broader distribution. The heavy olefinic stream may be hydroisomerized to form a distribution of different isomers. Further, the heavy olefinic stream may be finished to decrease unsaturated and aromatic compounds in the hydro-processed stream. In some examples, an intermediate olefinic stream is isolated from the intermediate stream and combined with the heavy olefinic stream for hydro-processing.

[0068] At block **212**, the hydro-processed stream is distilled to form a number of hydrocarbon fluids. Distilling the hydro-processed stream may include separating a distillate stream, a naphtha stream, or both from the hydro-processed stream. In some examples, the distillate stream is combined with the intermediate olefinic stream and processed to form final products, such as diesel fuel, gasoline, light lubricants, and other hydrocarbon fluids. Further, distilling the hydro-processed stream may include forming a heavy neutral oil stock stream, a medium neutral oil stock stream, or a light neutral oil stock stream, or any combinations thereof.

Examples

Analysis techniques

[0069] The gas chromatography analysis of compositions described herein was performed using a method to enable coverage up to C30. The column was 30 m long, with an inner diameter of 0.32 millimeters and a packing of 0.25 μm , available as a HP-5 column from Agilent. The carrier gas was nitrogen. The injector was held at a temperature of 150 °C and 10 psi. A 50 to 1 split ratio was used with a 121 mL per minute (mL/min) total flow rate and an injection size of 1 - 5 μL . The column oven was set to a 50 °C initial temp with a 10 °C/min ramp rate to a 320 °C final temperature. It was held at the 320 °C temperature for 8 minutes giving a total run time of 35 minutes. The detector was a flame ionization detector held at 300 °C, using a 30 mL/min flow of hydrogen, a 250 mL/min flow of air, and a 25 mL/min makeup stream of nitrogen. The gas chromatography analysis for dimerization or alkylation products was performed using a high temperature method to enable coverage up to C100. The column was 6 m long, with an inner diameter of 0.53 millimeters and a packing of 0.15 μm , available as a MXT-1 SimDist column from Restek company of State College, PA. The carrier gas was nitrogen. The injector was held at a temperature of 300 °C and 0.9 psi. A 15 to 1 split ratio was used with a 27.4 mL per minute (mL/min) total flow rate and an injection size of 1 μL . The column oven was set to an 80 °C initial temp with a 15 °C/min ramp rate to a 400 °C final temperature. It was held at the 400 °C temperature for 15 minutes giving a total run time of 36.3 minutes. The detector was a flame ionization detector held at 300 °C, using a 40 mL/min flow of hydrogen, a 200 mL/min flow of air, and a 45 mL/min makeup stream of nitrogen.

[0070] The C-13 NMR analysis was performed using a Bruker 400 MHz Advance III spectrophotometer. The samples were dissolved in chloroform-D (CDCl_3) or toluene-D8 in a 5 mm NMR tube at concentrations of between 10 to 15 wt. % prior to being inserted into the spectrophotometer. The C-13 NMR data was collected at room temperature (20 °C). The spectra were acquired with time averaging to provide a signal to noise level adequate to measure the signals of interest. Prior to data analysis, spectra were referenced by setting the chemical shift of the CDCl_3 solvent signal to 77.0 ppm.

[0071] H-1 NMR data was collected at room temperature. The data was recorded using a maximum pulse width of 45 degree, 8 seconds between pulses and signal averaging of 120 transients.

[0072] Simulated distillation (SimDist) was run using the techniques described in ASTM D2887 – 16a “Standard Test Method for Boiling Range Distribution of Petroleum Fractions by

Gas Chromatography.” The equipment used is further described herein with respect to the Gas Chromatography analyses.

Example 1: Composition of oligomerization feed stream after simple separation.

[0073] An example of the weight and volumetric composition of a oligomerization feed stream composition formed in the steam cracking of ethane, after separation with a primary fractionator, a caustic tower, and a drier, is shown in Table 1. This composition was determined by gas chromatography.

Table 1: Oligomerization feed stream composition after simple separation:

	Volume (%)
Hydrogen	44.2
Methane	6.37
Acetylene	1.19
Ethylene	36.4
Ethane	11.4
Propylene	0.48
Carbon Monoxide	0.03

Example 2: Synthesis of the heterogeneous catalyst material.

[0074] Catalysts containing from about 10 parts to about 90 parts of a zeolytic component and from about 90 parts to about 10 parts of a binder were combined on a calcined dry weight basis. The zeolytic component and binder dry powder was placed in a muller or a mixer and mixed for about 10 to 30 minutes. Sufficient water was added to the components during the mixing process to produce an extrudable paste. The extrudable paste was formed into a quadralobe or cylinder extrudate using an extruder. After extrusion, the extrudate was dried at a temperature ranging from about 250 °F to about 325 °F (168 °C). After drying, the dried extrudate was heated to about 1000 °F (538 °C) under flowing nitrogen. The extrudate was then cooled to ambient temperature and humidified with saturated air or steam. After the humidification, the extrudate was ion exchanged with about 0.5 to about 1 N ammonium nitrate solution. The ammonium nitrate solution ion exchange was repeated. The ammonium nitrate exchanged extrudate was then washed with deionized water to remove residual nitrate prior to calcination in air. After washing the wet extrudate, it was dried. The dried extrudate was then calcined for 3 h in a nitrogen/air mixture to a temperature of about 1000 °F (538 °C).

[0075] These catalysts may be used for the oligomerization of the oligomerization feed stream, which may include poisons, such as acetylene and carbon monoxide, in addition to

ethylene, propylene, hydrogen, methane, ethane, propane. The zeolitic component for the catalysts can include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-48, ZSM-50, ZSM-57, MCM-22, MCM-49, MCM-56, and numerous other zeolites. The binder may be selected from the group consisting of alumina, silica, titania, zirconia, tungsten oxide, ceria, niobia and combinations thereof.

Example 3: Oligomerization feed stream conversion to higher molecular weight products.

[0076] The capability of the heterogeneous catalyst with a zeolytic component to oligomerize the oligomerization feed stream was determined by testing the material in a batch reactor. The test included loading a dried catalyst into the reactor along with a liquid feed that could consist of 100 % alkane, such as decane or hexadecane, along with about 10 wt. % of an olefin, such as pentene or decene. The ratio of feed to catalyst was at a weight ratio of about 18 g/g. The reactor was inert purged with nitrogen while stirring. The ethylene oligomerization activity was evaluated by adding a pressurized gas feed containing either ethylene alone or a combination of ethylene, propylene, hydrogen, methane, ethane, propane, acetylene, and carbon monoxide as described with respect to Table 1. The mixture was then heated to between about 150 °C and about 250 °C while stirring for a designated amount of time, such as 24 to 72 hours. In this example, the reaction was performed for 48 hours. The reactor was run in semi-batch mode. The activity and selectivity was evaluated by analyzing the off-gas and liquid product composition.

[0077] **Fig. 3** is a plot 300 of the yield of different weight molecules, showing the changes as the catalyst is changed, in accordance with examples. An example reaction is the testing of 65 % zeolite and 35% alumina heterogeneous catalysts with a 10 wt. % decene / 90 wt. % hexadecane liquid feed at 225 °C and 200 psig total pressure for 48 hours with a 100% ethylene gas feed. After subtraction of the hexadecane feed, the simulated distillation by gas chromatography is shown in the plot of **Fig. 3**, which shows that the yield of 580 °F⁺ (304 °C⁺) diesel range molecules as well as 710 °F⁺ (376 °C⁺) base stock range molecules increases as the catalyst is switched from ZSM-48 to ZSM-5 to ZSM-11. The increase in yield of 710 °F⁺ (376 °C⁺) from below 30 % for ZSM-5 to above 35 % for ZSM-11 is particularly surprising because the zeolites have similar Si:Al₂ ratios of 29:1 (ZSM-5) and 26:1 (ZSM-11). As shown in **Fig. 3**, the result from the simulated distillation by gas chromatography on a feed with no catalyst present shows little to no conversion.

Example 4: Hydrogen impurity effects on oligomerization.

[0078] A 65 wt. % ZSM-5 and 35 wt. % alumina heterogeneous catalyst was tested with a 10 wt. % decene / 90 wt. % hexadecane liquid feed at 200 °C and 200 psig total pressure for 24

hours with one of two gas feeds, a 100 vol. % ethylene feed and a 50 vol. % ethylene / 50 vol. % hydrogen feed. After subtraction of the hexadecane feed, the simulated distillation by gas chromatography is shown in **Fig.4** for both gas feeds. There is little to no difference in the product distribution between the 100 % ethylene gas feed compared to the 50/50 ratio of ethylene to hydrogen feed. Accordingly, there is a significant economic incentive for not removing the hydrogen.

Example 5: Carbon monoxide and acetylene impurity effects on oligomerization.

[0079] **Fig. 4** is a plot 400 of a simulated distillation by gas chromatography comparing the products for a gas feed with hydrogen to a gas feed without hydrogen, in accordance with examples. A 65 % ZSM-11 and 35 % alumina heterogeneous catalyst was tested with a 10 wt. % decene / 90 wt. % hexadecane liquid feed at 200 °C and 200 psig total pressure for 48 hours with one of two gas feeds, a 100 vol. % ethylene feed, and a feed including 32.7 vol. % ethylene / 50 vol. % hydrogen / 10.6 vol. % ethane / 6.1 vol. % methane / 0.5 vol. % propylene / 0.1 vol. % carbon monoxide. After subtraction of the hexadecane feed, the simulated distillation by gas chromatography is shown in the plot of **Fig. 4** for both gas feeds. There is little to no difference in the product distribution between the 100 % ethylene gas feeds versus the impure feed. Accordingly, there is a significant economic incentive for not removing hydrogen and carbon monoxide as it avoids having to compress to 550 psig and the use of the cold box.

Example 6: Product characterization.

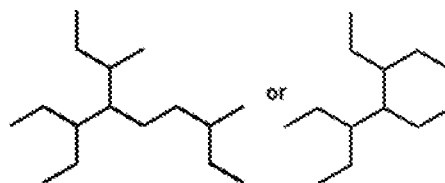
[0080] The liquid product was analyzed by DEPT-135 C-13 NMR to further investigate the product characteristics. The DEPT-135 C-13 NMR of the product that boiled above 700 °F showed a significant amount of branching via the low concentration of epsilon-CH₂ aliphatic carbons or linear methylenes in the product, as shown in further detail in Table 2. The branchiness is intrinsic to carbenium ion chemistry associated with Bronsted acid site olefin oligomerization over zeolites. While the product has a low viscosity index (VI) when compared to conventional base stock and almost no wax, the highly branched high molecular weight mixture has value as a quality hydrocarbon fluid and diesel fuel.

[0081] In addition, the ZSM-11 catalyst had significantly less branched, or more linear, products than ZSM-5 as indicated by the higher concentration of linear methylenes at almost constant methyl concentration. This is a surprising result as both catalysts have similar Si:Al₂ ratios of 29:1 (ZSM-5) and 26:1 (ZSM-11) and have 10-ring openings. The ZSM-11 has a slightly smaller openings, 5.3 Å x 5.4 Å, at its widest, compared to the three dimensional ZSM-

5's openings of 5.1 Å x 5.5 Å and 5.3 Å x 5.6 Å. This is described further in Table 2 along with examples of the structural features.

Table 2: Comparisons of branchiness for different catalysts

Catalyst Components	% epsilon-CH ₂	% CH ₃
Group III Base stock	23.3	14.9
65% ZSM-5 / 35% Alumina	13.3	21.7
65% ZSM-11 / 35% Alumina	19.1	21.6



Figs. 5(A) and 5(B) are plots of C-13 NMR spectra comparing a test product to a hydrocarbon fluid. The NMR in **Fig. 5(A)** is of a hydrocarbon fluid solvent consisting of mostly paraffins. The NMR in **Fig. 5(B)** is of a product made using a ZSM-5 oligomerization catalyst. The similarities indicate that boiling range cuts of the product may be useful as hydrocarbon fluids for industrial solvent applications.

Figs. 6(A) to 6(C) are 1-H NMR spectra comparing test products to a Group II hydrocarbon base stock. **Fig. 6(A)** is an NMR spectrum of the Group II base stock. **Fig. 6(B)** is a product spectrum formed using a ZSM-5 catalyst for oligomerization shows all the characteristic peaks of a Group II lube. The lower epsilon-CH₂ and higher CH₃ may decrease cold flow properties (such as Viscosity Index) but show the potential for base stock production. We also show a figure that shows a LN, MN, and HN lube base stock compared to the boiling point range of our ZSM-5 sample. All three materials could be produced from this material.

Embodiments

The embodiments of the present techniques include any combinations of the examples in the following numbered paragraphs.

1. A system for manufacturing a base stock from a light hydrocarbon stream, including a cracker configured to form a raw product stream from the light hydrocarbon stream, a separator configured to remove water from the raw product stream forming an oligomerization feed stream, and an oligomerization reactor configured to increase a molecular weight of the oligomerization feed stream forming a raw oligomer stream. The system also includes a distillation column configured to separate a heavy olefinic stream from the raw oligomer stream, a hydro-processing reactor configured to hydro-process the heavy olefinic stream to form a hydro-processed stream, and a product distillation column configured to separate the hydro-processed stream to form the base stock.

2. The system of embodiment 1, wherein the light hydrocarbon stream includes

ethane, butane, propane, or naphtha, or any combinations thereof.

[0087] 3. The system of either of embodiments 1 or 2, wherein the cracker includes a steam cracking reactor.

[0088] 4. The system of any of embodiments 1 to 3, wherein the separator includes a quench fractionator.

[0089] 5. The system of any of embodiments 1 to 4, including a primary fractionator configured to remove tar and steam cracking gas oil (SCGO) from the raw product stream, a caustic tower configured to remove hydrogen sulfide from the raw product stream, and a dryer configured to remove the water from the raw product stream.

[0090] 6. The system of any of embodiments 1 to 5, wherein the oligomerization reactor is configured to use a heterogeneous catalyst.

[0091] 7. The system of embodiment 6, wherein the heterogeneous catalyst includes a zeolite bound to a metal oxide.

[0092] 8. The system of any of embodiments 1 to 7, wherein the hydro-processing reactor includes a hydrocracking unit.

[0093] 9. The system of any of embodiments 1 to 8, wherein the hydro-processing reactor includes a hydroisomerization unit.

[0094] 10. The system of any of embodiments 1 to 9, wherein the product distillation column is configured to separate from the hydro-processed stream a distillate stream including naphtha, diesel fuel, and gasoline.

[0095] 11. The system of any of embodiments 1 to 10, wherein the product distillation column is configured to separate from the hydro-processed stream a heavy neutral stream, a medium neutral stream, and a light neutral stream.

[0096] 12. A method for manufacturing a base stock from a light hydrocarbon stream, including cracking the light hydrocarbon stream to form a raw product stream, removing water from the raw product stream to form an oligomerization feed stream, and oligomerizing the oligomerization feed stream to form an intermediate stream. The method also includes distilling a heavy olefinic stream from the intermediate stream, hydro-processing the heavy olefinic stream to form a hydro-processed stream, and distilling the hydro-processed stream to form the base stock.

[0097] 13. The method of embodiment 12, including separating naphtha, steam cracking gas oil (SCGO), or tar, or any combinations thereof, from the raw product stream.

[0098] 14. The method of either of embodiments 12 or 13, including separating hydrogen

sulfide from the raw product stream.

[0099] 15. The method of any of embodiments 12 to 14, including separating carbon dioxide from the raw product stream.

[0100] 16. The method of any of embodiments 12 to 15, wherein oligomerizing the oligomerization feed stream includes contacting the oligomerization feed stream with a heterogeneous catalyst including a zeolite bound with a metal oxide.

[0101] 17. The method of embodiment 16, including controlling a composition of the intermediate stream by changing a ratio of the zeolite to a metal oxide binder.

[0102] 18. The method of any of embodiments 12 to 17, including distilling a light linear alpha olefin stream from the intermediate stream.

[0103] 19. The method of any of embodiments 12 to 18, including distilling a heavy linear alpha olefin stream from the intermediate stream.

[0104] 20. The method of any of embodiments 12 to 19, wherein hydro-processing the heavy olefinic stream includes hydrocracking the heavy olefinic stream.

[0105] 21. The method of any of embodiments 12 to 20, wherein hydro-processing the heavy olefinic stream includes hydroisomerizing the heavy olefinic stream.

[0106] 22. The method of any of embodiments 12 to 21, wherein distilling the hydro-processed stream includes separating a distillate stream, a naphtha stream, or both from the hydro-processed stream.

[0107] 23. The method of any of embodiments 12 to 22, wherein distilling the hydro-processed stream includes forming a heavy neutral oil stock stream, a medium neutral oil stock stream, or a light neutral oil stock stream, or any combinations thereof.

[0108] 24. A system for manufacturing a base oil stock from a light hydrocarbon stream, including a steam cracker to form a raw product stream from the light hydrocarbon stream, a separator configured to remove naphtha, water, steam cracker gas oil (SCGO), and tar from the raw product stream to form an oligomerization feed stream, and an oligomerization reactor configured to convert the oligomerization feed stream to a higher molecular weight stream by contacting the oligomerization feed stream with a heterogeneous catalyst. The system also includes a distillation column configured to separate a heavy olefinic stream from the higher molecular weight stream, wherein the distillation column is configured to recover a light alpha-olefin stream from the higher molecular weight stream. A hydro-processing reactor is configured to demetallate the heavy olefinic stream, to crack the heavy olefinic stream, to form isomers in the heavy olefinic stream, or to hydrogenate olefinic bonds in the heavy olefinic stream, or any

combinations thereof. A product distillation column is configured to separate the isomers in the heavy olefinic stream to form a number of base stock streams.

[0109] 25. The system of embodiment 24, wherein the light hydrocarbon stream includes ethane.

[0110] 26. The system of either of embodiments 24 or 25, wherein the heterogeneous catalyst includes a zeolite bound with alumina.

[0111] While the present techniques may be susceptible to various modifications and alternative forms, the embodiments discussed above have been shown only by way of example. However, it should again be understood that the techniques is not intended to be limited to the particular embodiments disclosed herein. Indeed, the present techniques include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

CLAIMS:

1. A system for manufacturing a base stock from a light hydrocarbon stream, including a cracker configured to form a raw product stream from the light hydrocarbon stream, a separator configured to remove water from the raw product stream forming an oligomerization feed stream, and an oligomerization reactor configured to increase a molecular weight of the oligomerization feed stream forming a raw oligomer stream. The system also includes a distillation column configured to separate a heavy olefinic stream from the raw oligomer stream, a hydro-processing reactor configured to hydro-process the heavy olefinic stream to form a hydro-processed stream, and a product distillation column configured to separate the hydro-processed stream to form the base stock.
2. The system of claim 1, wherein the light hydrocarbon stream includes ethane, butane, propane, or naphtha, or any combinations thereof.
3. The system of either of claims 1 or 2, wherein the cracker includes a steam cracking reactor.
4. The system of any of claims 1 to 3, wherein the separator includes a quench fractionator.
5. The system of any of claims 1 to 4, including a primary fractionator configured to remove tar and steam cracking gas oil (SCGO) from the raw product stream, a caustic tower configured to remove hydrogen sulfide from the raw product stream, and a dryer configured to remove the water from the raw product stream.
6. The system of any of claims 1 to 5, wherein the oligomerization reactor is configured to use a heterogeneous catalyst.
7. The system of claim 6, wherein the heterogeneous catalyst includes a zeolite bound to a metal oxide.
8. The system of any of claims 1 to 7, wherein the hydro-processing reactor includes a hydrocracking unit.
9. The system of any of claims 1 to 8, wherein the hydro-processing reactor includes a hydroisomerization unit.
10. The system of any of claims 1 to 9, wherein the product distillation column is configured to separate from the hydro-processed stream a distillate stream including naphtha, diesel fuel, and gasoline.
11. The system of any of claims 1 to 10, wherein the product distillation column is configured to separate from the hydro-processed stream a heavy neutral stream, a medium neutral

stream, and a light neutral stream.

12. A method for manufacturing a base stock from a light hydrocarbon stream, including cracking the light hydrocarbon stream to form a raw product stream, removing water from the raw product stream to form an oligomerization feed stream, and oligomerizing the oligomerization feed stream to form an intermediate stream. The method also includes distilling a heavy olefinic stream from the intermediate stream, hydro-processing the heavy olefinic stream to form a hydro-processed stream, and distilling the hydro-processed stream to form the base stock.

13. The method of claim 12, including separating naphtha, steam cracking gas oil (SCGO), or tar, or any combinations thereof, from the raw product stream.

14. The method of either of claims 12 or 13, including separating hydrogen sulfide from the raw product stream.

15. The method of any of claims 12 to 14, including separating carbon dioxide from the raw product stream.

16. The method of any of claims 12 to 15, wherein oligomerizing the oligomerization feed stream includes contacting the oligomerization feed stream with a heterogeneous catalyst including a zeolite bound with a metal oxide.

17. The method of claim 16, including controlling a composition of the intermediate stream by changing a ratio of the zeolite to a metal oxide binder.

18. The method of any of claims 12 to 17, including distilling a light linear alpha olefin stream from the intermediate stream.

19. The method of any of claims 12 to 18, including distilling a heavy linear alpha olefin stream from the intermediate stream.

20. The method of any of claims 12 to 19, wherein hydro-processing the heavy olefinic stream includes hydrocracking the heavy olefinic stream.

21. The method of any of claims 12 to 20, wherein hydro-processing the heavy olefinic stream includes hydroisomerizing the heavy olefinic stream.

22. The method of any of claims 12 to 21, wherein distilling the hydro-processed stream includes separating a distillate stream, a naphtha stream, or both from the hydro-processed stream.

23. The method of any of claims 12 to 22, wherein distilling the hydro-processed stream includes forming a heavy neutral oil stock stream, a medium neutral oil stock stream, or a light neutral oil stock stream, or any combinations thereof.

24. A system for manufacturing a base oil stock from a light hydrocarbon stream, including a steam cracker to form a raw product stream from the light hydrocarbon stream, a separator configured to remove naphtha, water, steam cracker gas oil (SCGO), and tar from the raw product stream to form an oligomerization feed stream, and an oligomerization reactor configured to convert the oligomerization feed stream to a higher molecular weight stream by contacting the oligomerization feed stream with a heterogeneous catalyst. The system also includes a distillation column configured to separate a heavy olefinic stream from the higher molecular weight stream, wherein the distillation column is configured to recover a light alpha-olefin stream from the higher molecular weight stream. A hydro-processing reactor is configured to demetallate the heavy olefinic stream, to crack the heavy olefinic stream, to form isomers in the heavy olefinic stream, or to hydrogenate olefinic bonds in the heavy olefinic stream, or any combinations thereof. A product distillation column is configured to separate the isomers in the heavy olefinic stream to form a number of base stock streams.
25. The system of claim 24, wherein the light hydrocarbon stream includes ethane.
26. The system of either of claims 24 or 25, wherein the heterogeneous catalyst includes a zeolite bound with alumina.