Title: PREPARATION OF BRANCHED ALIPHATIC ALCOHOLS USING COMBINED PROCESS STREAMS FROM A HYDROGENATION UNIT, A DEHYDROGENATION UNIT, A DIMERIZATION UNIT AND AN ISOMERIZATION UNIT

Abstract: Systems and methods to produced branched aliphatic alcohols are described. Systems may include a hydrogenation unit, a dehydrogenation unit, an olefin dimerization unit, an olefin isomerization unit, a hydroformylation unit and/or combinations thereof. Methods for producing branched aliphatic alcohols may include dimerization and isomerization of olefins in a process stream. The isomerized olefins may be hydroformylated to produce aliphatic alcohols. After hydroformylation of the aliphatic alcohols, unreacted components from the hydroformylation process may be separated from the aliphatic alcohols products. The unreacted components from the hydroformylation process may be recycled back into the main process stream or sent to other processing units. Addition of multiple streams to the units may be performed to control reaction conditions in the units.
PREPARATION OF BRANCHED ALIPHATIC ALCOHOLS USING COMBINED PROCESS STREAMS FROM A HYDROGENATION UNIT, A DEHYDROGENATION UNIT, A DIMERIZATION UNIT AND AN ISOMERIZATION UNIT

Background

Cross Reference to Related Application

This application claims the benefit of U.S. Provisional Application Serial No. 60/511,452 filed October 15, 2003.

Field of Invention

The present invention generally relates to systems and methods for preparing aliphatic alcohols. More particularly, embodiments described herein relate to systems and methods for preparing branched aliphatic alcohols using a hydrogenation unit, a dehydrogenation unit, a dimerization unit, an isomerization unit and/or combinations thereof.

Description of Related Art

Aliphatic alcohols are important compounds that may be used in a variety of applications or converted to other chemical compounds (e.g., surfactants, sulfates).

Surfactants may be used in a variety of applications (e.g., detergents, soaps, oil recovery).

The structural composition of the aliphatic alcohol may influence the properties of the surfactant and/or detergent (e.g., water solubility, biodegradability and cold water detergency) produced from the aliphatic alcohol. For example, water solubility may be affected by the linearity of the aliphatic portion of the aliphatic alcohol. As the linearity of the aliphatic portion increases, the hydrophilicity (i.e., affinity for water) of the aliphatic alcohol surfactant may decrease. Thus, the water solubility and/or detergency performance of the aliphatic alcohol surfactant may decrease. Incorporating branches into the aliphatic portion of the aliphatic alcohol surfactant may increase the cold-water solubility and/or detergency of the aliphatic alcohol surfactant. Biodegradability, however, of the aliphatic alcohol surfactants may be reduced if the branches in the aliphatic portion of the alcohol surfactant include a high number of quaternary carbons. Incorporation of branches with a minimum number of quaternary carbon atoms into the aliphatic portion of the aliphatic alcohol surfactant may increase cold-water solubility and/or detergency of the alcohol surfactants while maintaining the biodegradability properties of the detergents.
The aliphatic portion of an aliphatic alcohol used to manufacture a surfactant may include one or more aliphatic alkyl groups as branches. Aliphatic alkyl groups that may form branches in the aliphatic portion may include methyl, ethyl, propyl or higher alkyl groups. Quaternary and tertiary carbons may be present when the aliphatic portion is branched. The number of quaternary and tertiary carbons may result from the branching pattern in the aliphatic portion. As used herein, the phrase “aliphatic quaternary carbon atom” refers to a carbon atom that is not bound to any hydrogen atoms.

The manufacture of a surfactant by oligomerizing C₃ and C₄ olefins is described by U.S. Patent No. 5,112,519 to Giacobbe et al., entitled “Process for Production of Biodegradable Surfactants and Compositions Thereof.”

A process to manufacture linear alcohols by dimerizing an olefin feed comprising C₆-C₁₀ linear olefins to obtain C₁₂-C₂₀ olefins is described by U. S. Patent No. 6,222,077 to Singleton et al., entitled “Dimerized Alcohol Compositions and Biodegradable Surfactants Made Therefrom Having Cold Water Detergency.” The dimerized olefins may be converted to alcohols by hydroformylation.

Processes to manufacture branched primary alcohol compositions are described by U.S. Patent No. 5,849,960 to Singleton et al. entitled “Highly Branched Primary Alcohol Compositions, and Biodegradable Detergents Made Therefrom” and U.S. Patent No. 6,150,322 to Singleton et al., entitled “Highly Branched Primary Alcohol Compositions, and Biodegradable Detergents Made Therefrom.”

Summary of the Invention

In an embodiment, aliphatic alcohols may be produced by a method that include hydrogenation of paraffins a feed stream containing olefins and paraffins may be processed in a hydrogenation unit. A process feed stream entering a hydrogenation unit may include linear olefins and paraffins having an average carbon number from 7 to 18. In an embodiment, a process feed stream entering a hydrogenation unit includes linear olefins and paraffins having an average carbon number from 10 to 17. As used herein, the phrase “carbon number” refers to the total number of carbon atoms in a molecule. A process feed stream entering a hydrogenation unit is derived, in some embodiments from a Fischer-Tropsch process.

In the hydrogenation unit at least a portion of the olefins in the feed stream may be hydrogenated to form paraffins. The resulting paraffinic feed stream may be fed into a
dehydrogenation unit. At least a portion of the paraffins in the feed stream may be dehydrogenated to form an olefin hydrocarbon stream. At least a portion of the olefinic hydrocarbon stream produced from the dehydrogenation unit may be fed into a dimerization unit.

In certain embodiments, a feed stream is fed into a dimerization unit that produces dimerized olefins. The produced dimerized olefins may include branched dimerized olefins. A process feed stream entering a dimerization unit is derived, in some embodiments, from a Fischer-Tropsch process. In an embodiment, produced dimerized olefins may be separated from the unreacted components after leaving the dimerization unit. The unreacted components, in some embodiments, may be recycled back into the dimerization unit.

Process conditions in the dimerization unit may be such that the resulting branched olefins have an average number of branches per olefin molecule from about 0.7 to about 2.5. The branched olefins may include, but are not limited to, methyl and/or ethyl branched olefins. A dimerization unit may produce branched olefins that include less than about 0.5 percent of quaternary carbon atoms. In an embodiment, a feed stream entering the dimerization unit includes alpha-olefins having an average carbon number from 4 to 9. The branched olefins produced from the dimerization of alpha-olefins having an average carbon number from 4 to 9 will have an average carbon number from 8 to 18.

The produced dimerized olefins may be converted to aliphatic alcohols. In some embodiments, dimerized olefins may be hydroformylated to produce aliphatic alcohols. After hydroformylation of the dimerized olefins, at least a portion of unreacted components from the hydroformylation process may be separated from the produced aliphatic alcohol products.

At least a portion of the unreacted components may be separated to produce an unreacted hydrocarbon stream and a produced dimerized olefins stream. At least a portion of the unreacted hydrocarbon stream may be recycled to the dimerization unit.

In an embodiment, an isomerization unit may be used to produce branched olefins. In an embodiment, at least a portion of the product stream exiting a dimerization unit may be combined with at least a portion of the product stream exiting an isomerization unit and the combined stream directed to a hydroformylation unit. At least a portion of the olefins in the combined stream may be hydroformylated in the hydroformylation unit to produce
aliphatic alcohols. After hydroformylation of the olefins, at least a portion of unreacted components from the hydroformylation process may be separated from the aliphatic alcohol products. At least a portion of the unreacted components may be separated.

Isomerization of olefins in a process stream may occur in an isomerization unit. In certain embodiments, a process feed stream entering an isomerization unit is derived from a Fischer-Tropsch process. At least a portion of the linear olefins in a process feed stream may be isomerized to branched olefins in the isomerization unit. The resulting branched olefins may have an average number of branches per olefin molecule from about 0.7 to about 2.5. The branched olefins may include, but are not limited to, methyl and/or ethyl branched olefins. The isomerization process may produce branched olefins that include less than about 0.5 percent of aliphatic quaternary carbon atoms.

In an embodiment, one or more hydrocarbon streams may be combined with the feed stream entering an isomerization unit. The hydrocarbon stream may be mixed with the feed stream to alter the concentration of the olefins entering the isomerization unit.

After the feed stream is processed in the isomerization unit, the resulting branched olefin-containing stream is passed into a hydroformylation unit. One or more hydrocarbon streams may be combined with the branched olefin-containing stream to alter the concentration of olefins entering the hydroformylation unit. After hydroformylation of the olefins, unreacted components from the hydroformylation process may be separated from the aliphatic alcohol products. Paraffins and unreacted olefins in the separated stream may be sent to a dehydrogenation unit.

In an embodiment, one or more hydrocarbons streams may be added with the feed streams entering an isomerization unit and/or a hydroformylation unit. The hydrocarbon stream may be mixed with the feed streams to alter the concentration of the olefins entering the isomerization unit and/or hydroformylation unit.

In certain embodiments, at least a portion of the aliphatic alcohols may be sulfated to form aliphatic sulfates. In some embodiments, aliphatic sulfates may include branched alkyl groups. In certain embodiments, at least a portion of the produced aliphatic alcohols may be oxyalkylated to form oxyalkyl alcohols. In some embodiments, oxyalkyl alcohols may include branched alkyl groups. In some embodiments, at least a portion of the produced branched aliphatic alcohols may be ethoxylated to form branched ethoxyalkyl
alcohols. At least a portion of the oxyalkyl alcohols may be sulfated to from oxyalkyl sulfates. In some embodiments, oxyalkyl sulfates may include branched alkyl groups.

**Brief Description of the Drawings**

Advantages of the present invention will become apparent to those skilled in the art with the benefit of the following detailed description of embodiments and upon reference to the accompanying drawings, in which:

FIG. 1 depicts a schematic diagram of an embodiment of a system for producing aliphatic alcohols using a hydrogenation unit, a dehydrogenation unit, a dimerization unit and an isomerization unit.

FIG. 2 depicts a schematic diagram of an embodiment of a separation unit to separate produced dimerized olefins from a reaction mixture.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawing and will herein be described in detail. It should be understood that the drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

**Detailed Description of Embodiments**

Hydrocarbon products may be synthesized from synthesis gas (i.e., a mixture of hydrogen and carbon monoxide) using a Fischer-Tropsch process. Synthesis gas may be derived by partial combustion of petroleum (e.g., coal, hydrocarbons), by reforming of natural gas or by partial oxidation of natural gas. The Fischer-Tropsch process catalytically converts synthesis gas into a mixture of products that includes saturated hydrocarbons, unsaturated hydrocarbons and a minor amount of oxygen-containing products. The products from a Fischer-Tropsch process may be used for the production of fuels (e.g., gasoline, diesel oil), lubricating oils and waxes.

Fischer-Tropsch process streams may also be used to prepare commodity products, which have economic value. For example, linear olefins are commodity products that are useful for the production of surfactants. Using a portion of the process stream to produce linear olefins may increase the economic value of a Fischer-Tropsch process stream.

Surfactants derived from branched olefins may have different properties than surfactants derived from linear olefins. For example, surfactants derived from branched
olefins may have increased water solubility and/or improved detergency properties compared to surfactants derived from linear olefins. Biodegradable properties of the surfactant, however, may be affected by the presence of quaternary carbon atoms in the branched portion of the surfactant. Surfactants made from branched olefins with a minimum number of quaternary carbon atoms may have similar biodegradable properties to surfactants derived from linear olefins. Production of branched olefins from a Fischer-Tropsch process stream may increase the economic value of the stream. In some embodiments, linear olefins may be converted into branched olefins with a minimum number of quaternary carbon atoms using an isomerization catalyst. Increasing the amount of branched olefins derived from a Fischer-Tropsch process stream may increase the economic value of the process streams.

Methods are described for increasing the amount of branched olefins derived from a process stream that includes certain amount of olefins, thus increasing the economic value of the process stream. Such methods are useful for both Fischer-Tropsch process streams and product streams from other sources that include hydrocarbons.

A hydrocarbon feed stream composition may include paraffins and olefins. At least a portion of the hydrocarbon stream may be made up of linear paraffins and olefins having at least 4 carbon atoms and up to 18 carbon atoms. A hydrocarbon feed stream may be obtained from a Fischer-Tropsch process or from an ethylene oligomerization process. Fischer-Tropsch catalysts and reaction conditions may be selected to provide a particular mix of products in the reaction product stream. For example, a Fischer-Tropsch catalyst and reaction conditions may be selected to increase the amount of olefins and decrease the amount of paraffins and oxygenates in the stream. Alternatively, the catalyst and reaction conditions may be selected to increase the amount of paraffins and decrease the amount of olefins and oxygenates in the stream.

The catalyst used in a Fischer-Tropsch process may be Mo, W, Group VIII compounds or combinations thereof. Group VIII compounds include, but are not limited to, iron, cobalt, ruthenium, rhodium, platinum, palladium, iridium and osmium. Combinations of Mo, W and Group VIII compounds may be prepared in the free metal form. In an embodiment, combinations of Mo, W and Group VIII compounds may be formed as alloys. Combinations of Mo, W and Group VIII compounds may be formed, in some embodiments, as oxides, carbides or other compounds. In other embodiments,
combinations of Mo, W and Group VIII compounds may be formed as salts. Iron based
and cobalt based catalysts have been used commercially as Fischer-Tropsch catalysts.
Ruthenium catalysts tend to favor the formation of high melting waxy species under high-
pressure conditions. Synthetic Fischer-Tropsch catalysts may include fused iron. In some
5 embodiments, a fused iron Fischer-Tropsch catalyst may include a promoter (e.g.,
potassium or oxides on a silica support, alumina support or silica-alumina support). Cobalt
metal may also be used in a Fischer-Tropsch catalyst. With the proper selection of
supports, promoters and other metal combinations, a cobalt catalyst may be tuned to
manufacture a composition enriched in the desired hydrocarbon species. Other catalysts,
such as iron-cobalt alloy catalysts, are known for their selectivity toward the production of
olefins. Catalysts and combinations for manufacture of hydrocarbon species by a Fischer-
Tropsch process are generally known.

While reference is made to a Fischer-Tropsch stream, any stream of olefins and
saturated hydrocarbons may be suitable. Many Fischer-Tropsch streams may contain from
5 percent to 80 percent olefins, the remainder being saturated hydrocarbons comprising
paraffins and other compounds. The Fischer-Tropsch stream may be separated into several
streams. For example, one stream may include hydrocarbons with an average carbon
number from 4 to 9 for streams used in a dimerization unit. A second stream may include
hydrocarbons with an average carbon number from 7 to 18 for processes that involve an
isomerization unit.

In some embodiments, feed streams containing olefins and paraffins are obtained
through cracking of paraffin wax or the oligomerization of olefins. Commercial olefin
products manufactured by ethylene oligomerization are marketed in the United States by
Chevron Phillips Chemical Company, Shell Chemical Company (as NEODENE®) and by
British Petroleum. Cracking of paraffin wax to produce alpha-olefin and paraffin feed
streams is described in U.S. Patent No. 4,579,986 to Sie, entitled “Process For The
Preparation Of Hydrocarbons” and U.S. Patent Application Serial No. 10/153,955 of
Ansorge et al., entitled “Process For The Preparation of linear Olefins and Use Thereof To
Prepare Linear Alcohols.” Specific procedures for preparing linear olefins from ethylene
are described in U.S. Patent No. 3,676,523 to Mason, entitled “Alpha-Olefin Production;”
3,737,475 to Mason, entitled “Alpha-Olefin Production” and U.S. Patent No. 4,020,121 to
Kister et al., entitled “Oligomerization Reaction System.” Most of the above-mentioned processes produce alpha-olefins. Higher linear internal olefins may be commercially produced (e.g., chlorination-dehydrochlorination of paraffins, paraffin dehydrogenation, isomerization of alpha-olefins).

In an embodiment, a feed stream is processed to produce a hydrocarbon stream that includes branched olefins. These branched olefins may be converted to branched aliphatic alcohols using various techniques. The feed stream may have a paraffin content range between about 50 percent by weight to about 90 percent by weight of the feed stream. In certain embodiments, a feed stream may have a paraffin content greater than about 90 percent by weight paraffins. The feed stream may also include olefins. The olefin content of the feed stream may be between about 10 percent by weight to about 50 percent by weight. In other embodiments, a feed stream may have an olefin content greater than 90 percent by weight olefins.

The composition of the feed stream may include hydrocarbons having an average carbon number ranging from 4 to 30. In an embodiment, an average carbon number of the hydrocarbons in a feed stream may range from 4 to 24. In other embodiments, an average carbon number of the feed stream may range from 4 to 18. An average carbon number of the hydrocarbons in a feed stream may range from 7 to 18 for processes that involve an isomerization unit. In certain embodiments, an average carbon number of the hydrocarbons in a feed stream may range from 10 to 17 for processes that involve an isomerization unit. In some embodiments, an average carbon number of hydrocarbons in a feed stream may range from 10 to 13 for processes that involve an isomerization unit. In other embodiments, an average carbon number of hydrocarbons in a feed stream may range from 14 to 17 for processes that involve an isomerization unit.

The average carbon number of the hydrocarbons in a feed stream may range from 4 to 9 for processes that use a dimerization unit. In certain embodiments, an average carbon number of the hydrocarbons in a feed stream ranges from 5 to 8 for processes that use a dimerization unit. In some embodiments, an average carbon number of hydrocarbons in a feed stream may range from 5 to 7. In other embodiments, an average carbon number of hydrocarbons in a feed stream may range from 7 to 9. A feed stream may include minor amounts of hydrocarbons having a carbon number that is higher or lower than the desired
carbon number range. In some embodiments, a feed stream may be derived from distillation of a process stream that includes a broader range of carbon numbers.

In an embodiment, a feed stream for a dimerization unit and/or an isomerization unit includes mono-olefins and/or paraffins. The mono-olefins may be of a linear or branched structure. The mono-olefins may have an alpha or internal double bond position. The feed stream may include olefins in which 50 percent or more of the olefin molecules present may be alpha-olefins of a linear (straight chain) carbon skeletal structure. In certain embodiments, at least about 70 percent of the olefins are alpha-olefins of a linear carbon skeletal structure. A hydrocarbon stream in which greater than about 70 percent of all of the olefin molecules are alpha-olefins of a linear carbon skeletal structure may be used in certain embodiments to convert olefins to aliphatic alcohols. Such a stream may be derived from a Fischer-Tropsch process. In some embodiments, a feed stream includes olefins in which at least about 50 percent of the olefin molecules present are internal olefins.

Branched chain olefins may be converted to branched aliphatic alcohols (e.g., branched primary alcohols) by a hydroformylation process. "Hydroformylation," as used herein, refers to the production of alcohols from olefins via a carbonylation and a hydrogenation process. Other processes may be used to produce aliphatic alcohols from olefins. Examples of other processes to produce aliphatic alcohols from olefins include, but are not limited to, hydrosilation, oxidation and hydrolysis, sulfation and hydration, and epoxidation and hydration. The composition of an alcohol product stream may include aliphatic alcohols having an average carbon number ranging from 5 to 31. In an embodiment, an average carbon number of the aliphatic alcohols in an alcohol product stream may range from 7 to 18. In certain embodiments, an average carbon number of the aliphatic alcohols in an alcohol product stream may range from 11 to 18. In some embodiments, an average carbon number of aliphatic alcohols in an alcohol product stream may range from 11 to 14. In other embodiments, an average carbon number of aliphatic alcohols in an alcohol product stream may range from 15 to 18.

In certain embodiments, a first hydrocarbon stream may contain unwanted compounds (e.g., oxygenates and dienes) that may reduce catalyst selectivity in a dimerization process used to produce aliphatic alcohols. Removal of the unwanted compounds may be performed by hydrogenation of the first hydrocarbon stream. Hydrogenation of the first hydrocarbon stream, in certain embodiments, may produce a
hydrocarbon stream that includes greater than about 90 percent paraffins. The hydrogenated hydrocarbon stream may be dehydrogenated to produce an olefinic stream. The catalyst used in the dehydrogenation process may control the position of the olefin double bond. In certain embodiments, an olefinic hydrocarbon stream may include olefins in which greater than 70 percent of the olefins are alpha-olefins of a linear carbon skeletal structure. In other embodiments, an olefinic hydrocarbon stream may include olefins in which 50 percent or more of the olefin molecules present may be internal olefins.

Referring to System 100 as depicted in FIG. 1, a first hydrocarbon stream may be introduced into hydrogenation unit 110 via first conduit 112. The first hydrocarbon stream includes olefins and paraffins. Hydrocarbons in the first hydrocarbon stream may have an average carbon number from 4 to 9. In certain embodiments, hydrocarbons in a first hydrocarbon stream may have an average carbon number from 5 to 8. In some embodiments, hydrocarbons in a first hydrocarbon stream may have an average carbon number from 5 to 7. In other embodiments, hydrocarbons in a first hydrocarbon stream may have an average carbon number from 5 to 9. In hydrogenation unit 110, at least a portion of the olefins in the first hydrocarbon stream may be hydrogenated to paraffins to produce a second hydrocarbon stream.

Reaction conditions in hydrogenation unit 110 may be controlled to hydrogenate olefins and dienes and to remove oxygenates. An operating temperature of hydrogenation unit 110 may range between about 100 °C and about 300 °C. In some embodiments, an operating temperature may range between about 150°C and about 275 °C. In other embodiments, an operating temperature may range between about 175 °C and 250 °C. An operating pressure may range from about 5 atmospheres (506 kPa) to about 150 atmospheres (1520 kPa). In some embodiments, an operating pressure may range from 10 atmospheres psi (1013 kPa) to about 50 atmospheres (5065 kPa).

Hydrogenation processes may be carried out using any type of catalyst bed arrangement (e.g., fluidized bed, moving bed, slurry phase bed or a fixed bed). In certain embodiments, a fixed bed arrangement may be used. In a fixed bed system, hydrogen may be supplied to the hydrogenation stage at a gas hourly space velocity in the range from about 100 normal liter gas/liter catalyst/hour (NL/L/hr) to about 1000 NL/L/hr. In some embodiments, hydrogen may be supplied at a gas hourly space velocity in the range from about 250 NL/L/hr to 5000 NL/L/hr. "Gas space velocity as expressed in units of normal
liter of gas/liter of catalyst/hour,” as used herein, is the volume of a gas in liters at standard conditions of 0 °C and 760 mm Hg.

Hydrogenation catalysts are generally known and are commercially available in a large variety of compositions. In some embodiments, a hydrogenation catalyst may include one or more metals from Groups VIb and VII of the periodic Table of the Elements. In certain embodiments, metals may include, but are not limited to, molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. The hydrogenation catalyst may include a refractory oxide or a silicate as a binder.

Hydrogenation reaction conditions and catalysts are described in European Patent No. 0 583 836 to Eilers et al., entitled “Process For The Preparation of Hydrocarbon Fuels;” European Patent No. 0 668 342 to Eilers et al., entitled “Lubricating Base Oil Preparation Process.” Hydrogenation reaction conditions and catalysts are also described in U.S. Patent No. 5,371,308 to Gosselink et al., entitled “Process For The Preparation Of Lower Olefins.”

At least a portion of the second hydrocarbon stream may exit hydrogenation unit 110 and enter dehydrogenation unit 114 via second conduit 116. At least a portion of the unreacted paraffins in the second hydrocarbon stream may be dehydrogenated to produce an olefinic hydrocarbon stream by use of a catalyst selected from a wide range of catalyst types. For example, the catalyst may be based on a metal or metal compound deposited on a porous support. The metal or metal compound may be selected from, but is not limited to, chrome oxide, iron oxide and noble metals.

Techniques of preparing catalysts, for performing the dehydrogenation step and for performing associated separation steps are known in the art. For example, suitable procedures for preparing catalysts and performing the dehydrogenation step are described in U.S. Patent No. 5,012,021 to Vora et al., entitled “Process For the Production of Alkyl Aromatic Hydrocarbons Using Solid Catalysts;” U.S. Patent No. 3,274,287 to Moore et al., entitled “Hydrocarbon Conversion Process and Catalyst;” U.S. Patent No. 3,315,007 to Abell et al., entitled “Dehydrogenation of Saturated Hydrocarbons Over Noble-Metal Catalyst;” U.S. Patent No. 3,315,008 to Abell et al., entitled “Dehydrogenation of Saturated Hydrocarbons Over Noble-Metal Catalyst;” U.S. Patent No. 3,745,112 to Rausch, entitled “Platinum-Tin Uniformly Dispersed Hydrocarbon Conversion Catalyst and Process;” U.S. Patent No. 4,506,032 to Imai et al., entitled “Dehydrogenation Catalyst Composition” and
U.S. Patent No. 4,430,517 to Imai et al., entitled “Dehydrogenation Process Using a Catalytic Composition.”

Reaction conditions in dehydrogenation unit 114 may be varied to control unwanted side products (e.g., coke, dienes, oligomers, cyclized hydrocarbons) and control double bond position in the olefin. In certain embodiments, temperatures may range from greater than about 300 °C to less than about 700 °C. In other embodiments, a reaction temperature may range from about 450 °C to about 550 °C. During the dehydrogenation reaction, the pressures in dehydrogenation unit 114 may range from greater 0.010 atmosphere (1 kPa) to about 25.0 atmospheres (2534 kPa). In an embodiment, a total pressure of dehydrogenation unit 114 during the reaction may range from about 0.010 atmosphere (1 kPa) to about 15.0 atmospheres (15200 kPa). In certain embodiments, pressure in dehydrogenation unit 114 may range from about 1.0 atmosphere (101 kPa) to about 5.0 atmospheres (510 kPa). In some embodiments, hydrogen may be fed into dehydrogenation unit 114 together with the paraffins and unreacted olefins stream in order to prevent coke from forming. The hydrogen to paraffins molar ratio may be set between about 0.1 moles of hydrogen to about 20 moles of paraffins. In some embodiments, hydrogen to paraffin molar ratio is about 1 to 10.

The amount of time (e.g., the residence time) that a process stream remains in dehydrogenation unit 114 may determine, to some extent, the amount of olefins produced. Generally, the longer a process stream remains in dehydrogenation unit 114, the conversion level of paraffins to olefins increases until an olefin-paraffin thermodynamic equilibrium is obtained. The residence time of the paraffins and unreacted olefins stream in dehydrogenation unit 114 may be selected such that the conversion level of paraffins to olefins may be kept below 50 mole percent. In certain embodiments, a conversion level of paraffins to olefins may be kept in the range from 5 to 30 mole percent. By keeping the conversion level low, side reactions may be prevented (e.g., diene formation and cyclization reactions).

In certain embodiments, at least a portion of non-converted paraffins may be separated from a third hydrocarbon stream using generally known techniques. Such separation may be accomplished by extraction, distillation or adsorption techniques. The paraffins may be recycled to dehydrogenation unit 114 to undergo dehydrogenation to continue the process to produce aliphatic alcohols.
At least a portion of the third hydrocarbon steam may exit the dehydrogenation unit 114 and enter dimerization unit 118 via third conduit 120. In dimerization unit 118, at least a portion of the olefins in the third hydrocarbon stream may be dimerized. The resulting dimerized olefins and the unreacted hydrocarbons in the third hydrocarbon stream may exit dimerization unit 118 as a fourth hydrocarbon stream.

A dimerization catalyst used in dimerization unit 118 may be a homogeneous or heterogeneous catalyst. In certain embodiments, a dimerization catalyst used in dimerization unit 118 may be a catalyst that includes oxides of Group III, Group IVA, Group IVB, Group VIIIA, or combinations thereof. Examples of such oxides include, but are not limited to, nickel oxide, silicon dioxide, titanium dioxide, aluminum oxide or zirconium dioxide. The dimerization catalyst may include an amorphous nickel oxide (NiO) present as a dispersed substantial monolayer on the surfaces of a silica (SiO₂) support. The silica support may also include on the surface minor amounts of an oxide of aluminum, gallium or indium such that the ratio of nickel oxide to metal oxide present in the catalyst is within the range from about 4:1 to about 100:1. The dimerization catalyst may be prepared by precipitating a water insoluble nickel salt onto the surface of a silica support. The silica support may be impregnated with a metal oxide. In other embodiments, a dimerization catalyst may be prepared by precipitating a water insoluble nickel salt onto a silica-alumina support. The silica-alumina support may be dealuminized such that the resulting nickel oxide/alumina ratio falls within the range from about 4:1 to about 100:1. The catalyst may be activated by calcination in the presence of oxygen at a temperature with a temperature range from about 300 °C to about 700 °C. In some embodiments, the catalyst may be activated by calcination in the presence of oxygen at a temperature with a temperature range from about 500 °C to about 600 °C.

Silica useful as a support material may have a surface area within a range from about 100 m²/g to about 450 m²/g. In an embodiment, a silica surface area may be within the range from about 200 m²/g to about 400 m²/g. A range of nickel oxide content may be from about 7 percent to about 70 percent by weight. In certain embodiments, a nickel oxide content may be from about 20 percent to about 50 percent by weight, depending on the surface area of the particular support utilized in preparing the catalyst. For a silica support having a surface area of about 300 m²/g, a nickel oxide content may, in some
embodiments, range from about 21 percent to about 35 percent by weight. A nickel oxide content may, in other embodiments, be about 28 percent by weight.

The silica support may be in dry granular form or in a hydrogel form prior to precipitation of the nickel oxide precursor compound on the surfaces thereof. Silica hydrogel may be prepared by mixing a water-soluble silicate, (e.g., a sodium or potassium silicate) with a mineral acid. The water-soluble silicate may be washed with water to remove water-soluble ions. The resulting silica hydrogel may be partially dried. In some embodiments, a silica hydrogel may be completely dried.

A nickel oxide precursor may include a water-insoluble nickel salt, such as nickel carbonate, nickel phosphate, nickel nitrate or nickel hydroxide. A water-insoluble nickel salt may be generated in-situ by forming an aqueous mixture of the silica gel and a water-soluble nickel salt. The nickel salt may include, but is not limited to, nickel nitrate, nickel sulfonate, nickel carbonylate, nickel halide. A base may be added to the aqueous mixture to induce precipitation of the water-insoluble nickel salt. The water-insoluble nickel salt may be precipitated in finely divided form within the interstices and on the surface of the silica support. The treated silica support may then be recovered, washed several times and dried.

A second component in the catalyst may be a trivalent metal oxide, which may include, but is not limited to, aluminum, gallium and indium or combinations thereof.

Although a nickel oxide and/or silica catalyst may be active for olefin dimerization, it may deactivate quickly. Deactivation may be from formation of large oligomers that remain attached to the catalyst surface. Large oligomers may act as coke precursors, in some embodiments. A presence of a small amount of the trivalent metal oxide within the catalyst may form acid sites. Acidic sites may promote catalytic activity without promoting unwanted and/or excessive oligomer formation.

A trivalent metal oxide may be incorporated into the silica support by generally known techniques (e.g., precipitation, impregnation). In an embodiment, a trivalent metal oxide may be impregnated into the silica support as an aqueous solution by the addition of a water-soluble salt. The water-soluble metal salt may include, but is not limited to, metal nitrates, metal chlorides or metal sulfates. Once impregnated with a metal salt, the silica support may be dried and calcinated to reduce the metal salt to the oxide form. The silica-
trivalent oxide support may further treated to incorporate a nickel oxide layer onto the silica-trivalent metal oxide support.

In an embodiment, silica-trivalent metal oxide (e.g., silica/alumina, silica/gallia or silica/india gel) may be utilized as support material. In certain embodiments, a content of metal oxide (e.g., alumina) present in the support may be low in comparison with the content of nickel oxide. Dealumination of the silica/alumina gel of relatively high alumina content (e.g., above about 5 percent by weight) may be necessary to reduce the content of alumina. Dealumination may be accomplished by known techniques (e.g., extraction of the aluminum with an organic or inorganic acid). Organic or inorganic acids may include, but are not limited to, nitric acid, sulfuric acid, hydrochloric acid, chloroacetic acid or ethylene diamine tetraacetic acid. Extraction may be accomplished by adding the acid to an aqueous dispersion of the aluminio silicate followed by stirring, decantation and washing with water. The process may be repeated one or more times until the desired alumina content is achieved. The solids are then dried, calcined and further treated to incorporate the nickel oxide layer onto the silica/alumina support.

A content of trivalent metal oxide with respect to the content of the nickel oxide present in the silica support may be significant. In certain embodiments, when the content of trivalent metal oxide is too low (e.g., above a nickel oxide to trivalent metal oxide ratio of about 100 to 1) then the yield of dimer decreases and the catalyst may tend to deactivate quickly. In certain embodiments, a content of trivalent metal oxide may be high (e.g., below a nickel oxide to trivalent metal oxide ratio of about 4 to 1). A high trivalent metal oxide content may lower the yield of dimer. In some embodiments, a high trivalent metal oxide content may raise an average content of methyl branching in the dimerized olefin product. In certain embodiments, a content of trivalent metal oxide may be such that the ratio of nickel oxide to trivalent metal oxide falls within the range from about 4:1 to about 30:1. In other embodiments, a content of trivalent metal oxide may be such that the ratio of nickel oxide to trivalent metal oxide is between about 5:1 to about 20:1. In certain embodiments, a ratio of nickel oxide to trivalent metal oxide may be between about 8:1 to about 15:1.

In certain embodiments, a dimerization catalyst may contain from about 21 percent to about 35 percent by weight of nickel oxide and about 1 percent to about 5 percent by weight of trivalent metal oxide, based on the total weight of nickel oxide, trivalent metal
oxide and silica. In certain embodiments, a dimerization catalyst may include from about 1.5 percent to about 4 percent by weight trivalent metal oxide based on the total weight of nickel oxide, trivalent metal oxide and silica.

Preparation of dimerization catalysts are described in U.S. Patent No. 5,849,972 to Vicari et al., entitled “Oligomerization Of Olefins To Highly Linear Oligomers, and Catalyst For This Purpose,” and U.S. Patent No., 5,169,824 to Saleh et al., entitled “Catalyst Comprising Amorphous NiO On Silica/Alumina Support.”

Depending on the choice of catalyst, the resulting dimer may be branched. The branches of the olefin produced in dimerization unit 118 may include methyl, ethyl and/or longer carbon chains. In an embodiment, dimerized olefins may contain greater than about 50 percent methyl branches. In certain embodiments, dimerized olefins may contain greater than about 90 percent methyl branches. The dimerized olefins may be separated from the unreacted products through techniques known in the art. One such technique is fractional distillation.

Conversion of olefins to dimers in dimerization unit 118, may be carried out as a batch, continuous (e.g., using a fixed bed), semi-batch or multi-step process. In a batch process, the catalyst may be slurried with the first hydrocarbon feed stream. Temperature conditions for the dimerization reaction may range from about 120 °C to about 200 °C. In an embodiment, a reaction temperature may range from about 150 °C to about 165 °C.

Reaction temperatures may be controlled with evaporative cooling (e.g., the evaporation of lighter hydrocarbon fractions from the reaction mixture may control the reaction temperature).

Produced dimerized olefins may be separated, if desired, from the reaction mixture through techniques known in the art (e.g., distillation, adsorption/desorption and/or molecular sieves). Referring to FIG. 2, a fourth hydrocarbon stream may exit dimerization unit 118 and enter separation unit 122 via separation conduit 124. Separation unit 122 may produce at least two streams, a branched olefins stream and a linear olefins and paraffins stream. In separation unit 122, the fourth hydrocarbon stream may be contacted with organic and/or inorganic molecular sieves (e.g., zeolite or urea) with the correct pore size for branched olefins and/or linear olefins and paraffins. Subsequent desorption (e.g., solvent desorption) of at least a portion of the branched olefins and/or at least a portion of
the linear olefins and paraffins from the molecular sieves may produce at least two streams (e.g., a branched olefins stream and a linear olefins and paraffins stream).

Separation unit 122 may include a fixed bed containing adsorbent for separation of the fourth hydrocarbon stream to produce a branched olefin and paraffins stream and a linear olefins and paraffins stream. Separation temperatures in separation unit 122 may range from about 100 °C to about 400 °C. In some embodiments, separation temperatures may range from about 180 °C to about 380 °C. Separation in separation unit 122 may be conducted at a pressure ranging from about 2 atmospheres (202 kPa) to about 7 atmospheres (710 kPa). In some embodiments, a pretreatment of a fourth hydrocarbon stream may be performed to prevent adsorbent poisoning. An example of an adsorption/desorption process is a Molex process using Sorbex® separations technology (UOP process, UOP, Des Plaines, IL). Adsorption/desorption processes are described in U.S. Patent No. 6,225,518 to Sohn et al., entitled “Olefinic Hydrocarbon Separation Process;” U.S. Patent No. 5,292,990 to Kantner et al., entitled, “Zeolite Compositions For Use in Olefinic Separations” and U.S. Patent No. 5,276,246 to McCulloch et al., entitled “Process For Separating Normal Olefins From Non-Normal Olefins.”

At least a portion of the linear olefins and paraffins stream may be transported to other processing units and/or stored on site. The paraffins and unreacted olefins stream may contain hydrocarbons with a carbon number less than 9. In an embodiment, at least a portion of the linear olefins and paraffins stream may be combined with the second hydrocarbon stream in second conduit 116 via linear olefin and paraffin recycle conduit 126. The combined stream may enter dehydrogenation unit 114 via second conduit 116 to continue the process to produce aliphatic alcohols. In some embodiments, a linear olefins and paraffins stream may be introduced directly into dehydrogenation unit 114.

At least a portion of the branched olefins stream may be transported and utilized in other processing streams and/or stored on site via branched olefins conduit 128. The paraffins and unreacted olefins stream may contain hydrocarbons with a carbon number less than about 8. In some embodiments, at least a portion of a branched olefins stream may exit separation unit 122 and be introduced into fourth conduit 130 via branched olefins conduit 128. In other embodiments, at least a portion of a branched olefins stream may exit separation unit 122 and be introduced directly into hydroformylation unit 132.
At least a portion of the fourth hydrocarbon stream may exit dimerization unit 118 and be introduced into hydroformylation unit 132 via fourth conduit 130. The fourth hydrocarbon stream includes branched olefins. At least a portion of the olefins in the fourth hydrocarbon stream may be hydroformylated to produce aliphatic alcohols.

In certain embodiments, a hydrocarbon stream from a dimerization unit may be combined with a hydrocarbon stream from an isomerization unit to produce a combined stream. The combined stream may be introduced into a hydroformylation unit. Combining streams from the two units may result in a more economically valuable process to produce branched aliphatic alcohols. A sixth hydrocarbon stream may be introduced directly into hydroformylation unit 132 through one or more hydroformylation unit ports. At least a portion of a sixth hydrocarbon stream may be introduced into fourth conduit 130 via fifth conduit 134 upstream of hydroformylation unit 124 to produce a combined stream. The sixth hydrocarbon stream may be a stream exiting from isomerization unit 136.

Isomerization unit 136 may be fed by a fifth hydrocarbon stream containing paraffins and unreacted olefins via sixth conduit 138. In isomerization unit 136, at least a portion of the olefins in the fifth hydrocarbon stream may be isomerized to branched olefins to produce the sixth hydrocarbon stream. A fifth hydrocarbon stream may include hydrocarbons with an average carbon number from 7 to 18. In certain embodiments, a fifth hydrocarbon stream may include hydrocarbons with an average carbon number from 10 to 17. In some embodiments, a fifth hydrocarbon stream may include hydrocarbons with an average carbon number from 10 to 13. In other embodiments, a fifth hydrocarbon stream may include hydrocarbons with an average carbon number from 14 to 17. In some embodiments, a fifth hydrocarbon stream includes alpha-olefins. In certain embodiments, a fifth hydrocarbon stream is a stream derived from a Fischer-Tropsch process. The alpha-olefin content of the fifth hydrocarbon stream may be greater than about 70 percent of the total amount of olefins in the third hydrocarbon stream. In isomerization unit 136, at least a portion of the olefins in the fifth hydrocarbon stream may be isomerized to branched olefins (e.g., isoolefins) to produce a sixth hydrocarbon stream.

In certain embodiments, isomerization unit 136 may have several points of entry to accommodate process streams, which may vary in composition. Process streams may be from other processing units and/or storage units. Examples of process streams include, but are not limited to, a diluent hydrocarbon stream, and/or other hydrocarbon streams that
include olefins and paraffins derived from other processes. As used herein, “entry into the isomerization unit” refers to entry of process streams into the isomerization unit through one or more entry points.

Conditions for olefin isomerization in isomerization unit 136 may be controlled such that the number of carbon atoms in the olefins before and after the isomerization is substantially the same. Process conditions to skeletally isomerize linear olefins to branched olefins are described in U. S. Patent No. 5,648,584 to Murray, entitled “Process for Isomerizing Linear Olefins to Isolefins” and U.S. Patent No. 5,648,585 to Murray et al., entitled “Process for Isomerizing Linear Olefins to Isolefins.”

In an embodiment, linear olefins in a fifth hydrocarbon stream are isomerized in isomerization unit 136 by contacting at least a portion of the fifth hydrocarbon stream with a zeolite catalyst. The zeolite catalyst may have at least one channel with a crystallographic free channel diameter ranging from greater than 4.2 Å and less than about 7 Å. The zeolite catalyst may have an elliptical pore size large enough to permit entry of a linear olefin and diffusion, at least partially, of a branched olefin. The pore size of the zeolite catalyst may also be small enough to retard coke formation.

Olefin isomerization may be conducted in isomerization unit 136 at temperatures ranging from about 200 °C to about 500 °C. Temperatures in isomerization unit 136 are, in some embodiments, kept below the temperature at which the olefin will crack extensively. As used herein, “cracking” refers to the process of thermally degrading molecules into smaller molecules. To inhibit cracking, low temperatures may be used at low feed rates. In certain embodiments, lower temperatures may be used when the amount of oxygenates present in the process stream is low. Higher feed rates may be desirable to increase the production rate of isomerised products. Higher feed rates may be used, in some embodiments, when operating at higher reaction temperatures. The reaction temperature, however, should be set such that cracking to lower boiling weight products is minimized. For example, greater than 90 percent of linear C_{12}-C_{14} olefins may be converted to branched olefins at 230 °C at a feed rate of 60 grams per hour per 6 grams of catalyst with minimal cracking. Pressures maintained in isomerization unit 136 may be at a hydrocarbon partial pressure ranging from about 0.1 atmospheres (10 kPa) to about 20 atmospheres (2026 kPa). In an embodiment, a partial pressure may range from above about 0.5 atmospheres (51 kPa) to about 10 atmospheres (1013 kPa).
In an embodiment, a seventh hydrocarbon stream may be introduced into hydroformylation unit 132 through one or more hydroformylation ports. In certain embodiments, at least a portion of a seventh hydrocarbon stream may be introduced into fourth conduit 130 upstream of hydroformylation unit 132 via seventh conduit 140 to produce a combined stream. The combined stream may enter hydroformylation unit 132 and at least a portion of the olefins in the combined stream may be hydroformylated to produce a hydroformylation reaction stream. In an embodiment, a paraffin content of the seventh hydrocarbon stream may be greater than about 50 percent and less than about 99 percent relative to the total hydrocarbon content. In certain embodiments, a paraffin content of the seventh hydrocarbon stream may be between about 60 percent and about 90 percent relative to the total hydrocarbon content. In an embodiment, an olefin content of a seventh hydrocarbon stream ranges between about 1 percent and about 99 percent relative to the total hydrocarbon content. In certain embodiments, an olefin content of a seventh hydrocarbon stream ranges between about 45 percent and about 95 percent. In other embodiments, an olefin content of a seventh hydrocarbon stream may be greater than 80 percent relative to the total hydrocarbon stream.

In certain embodiments, at least a portion of an eighth hydrocarbon stream may be introduced into sixth conduit 138 upstream of isomerization unit 136 via eighth conduit 142 to produce a combined stream. The combined stream may enter isomerization unit 136 and at least a portion of the olefins in the combined stream may be isomerized to produce a sixth hydrocarbon stream. In an embodiment, a paraffin content of the eighth hydrocarbon stream may be greater than about 50 percent and less than about 99 percent relative to the total hydrocarbon content. In certain embodiments, a paraffin content of the eighth hydrocarbon stream may be between about 60 percent and about 90 percent relative to the total hydrocarbon content. In an embodiment, an olefin content of an eighth hydrocarbon stream ranges between about 1 percent and about 99 percent relative to the total hydrocarbon content. In certain embodiments, an olefin content of an eighth hydrocarbon stream ranges between about 45 percent and about 95 percent. In other embodiments, an olefin content of an eighth hydrocarbon stream may be greater than 80 percent relative to the total hydrocarbon stream.

The sixth and seventh hydrocarbon streams may be used to regulate the olefin concentration in hydroformylation unit 132 at a concentration sufficient to maximize
hydroformylation of the olefin. The sixth and seventh hydrocarbon streams may be, but are not limited to, a hydrocarbon stream containing olefin, paraffins and/or hydrocarbon solvents.

A combined stream may include, but is not limited to, a fourth hydrocarbon stream, a sixth hydrocarbon stream, a seventh hydrocarbon stream and/or combinations thereof, may be introduced into hydroformylation unit 132 via fourth conduit 130. An advantage of combining the streams may be that overall production of aliphatic alcohols may be increased with fewer throughputs. At least a portion of the olefins in the combined stream may be hydroformylated to produce aliphatic alcohols.


A hydroformylation catalyst used in hydroformylation unit 132 may include a metal from Group VIII of the Periodic Table. Examples of Groups VIII metals include cobalt, rhodium, nickel, palladium or platinum. The Group VIII metal may be used as a complex compound. A complex compound may be a Group VIII metal combined with a ligand. Examples of ligands include, but are not limited to, a phosphine, phosphite, arsine, stibine or pyridine ligand. Examples of hydroformylation catalysts include, but are not limited to, cobalt hydrocarbonyl catalyst, cobalt-phosphine ligand catalyst, rhodium-phosphine ligand catalyst or combinations thereof.

In hydroformylation unit 132, olefins may be hydroformylated using a continuous, semi-continuous or batch process. In case of a continuous mode of operation, the liquid hourly space velocities may be in the range of about 0.1 h⁻¹ to about 10 h⁻¹. When operating hydroformylation unit 132 as a batch process, reaction times may vary from about 0.1 hours to about 10 hours or even longer.

Reaction temperatures in hydroformylation unit 132 may range from about 100 °C to about 300 °C. In certain embodiments, reaction temperatures in the hydroformylation unit ranging from about 125 °C to about 250 °C may be used. Pressure in hydroformylation unit 132 may range from about 1 atmosphere (101 kPa) to about 300 atmospheres (30398 kPa). In an embodiment, a pressure from about 20 (2027 kPa) to about 150 atmospheres (15199 kPa) may be used. An amount of catalyst relative to the amount of olefin to be hydroformylated may vary. Typical molar ratios of catalyst to olefin in the hydrocarbon stream may range from about 1:1000 to about 10:1. A ratio of between about 1:10 and about 5:1 may be used in certain embodiments. In an embodiment, a
second stream may be added to hydroformylation unit 132 to control reaction conditions. The second stream may include solvents that do not interfere substantially with the desired reaction. Examples of such solvents include, but are not limited to, alcohols, ethers, acetonitrile, sulfolane and paraffins.

Mono-alcohol selectivities of at least 90 percent and even of at least 92 percent may be achieved in hydroformylation unit 132. In addition, olefin conversions to aliphatic alcohols may range from about 50 percent by weight to greater than about 95 percent by weight. In certain embodiments, olefin conversion to aliphatic alcohols may be greater than 75 percent by weight. In some embodiments, olefin conversion to aliphatic alcohols may be greater than about 99 percent by weight.

Isolation of aliphatic alcohols produced from the hydroformylation reaction product stream may be achieved by generally known methods. In an embodiment, isolation of the aliphatic alcohols includes subjecting the produced aliphatic alcohols to a first distillation, a saponification, a water washing treatment and a second distillation.

The hydroformylation reaction mixture stream may enter separator 144 via ninth conduit 146. In separator 144, the hydroformylation reaction product stream may be subjected to a first distillation step (e.g., flash distillation or a short path distillation). In an embodiment, a short path distillation may be used to produce at least two streams, a bottom stream and a top stream. At least a portion of the bottom stream may be recycled to hydroformylation unit 132 via bottom stream recycle conduit 148, in certain embodiments. The top stream may include, but is not limited to, paraffins, unreacted olefins and a crude aliphatic alcohol product.

In an embodiment, a top stream may be subjected to a saponification treatment to remove any acids and esters present in the stream. Saponification may be performed by contacting the top stream with an aqueous solution of a hydroxide base (e.g., sodium hydroxide or potassium hydroxide) at elevated temperatures with agitation. The saponification may be carried out by contacting the top stream with an aqueous 0.5 percent to 10 percent hydroxide base solution at a crude alcohol/water ratio of 10:1 to 1:1. The amount of hydroxide base used may depend on an estimated amount of esters and acids present.

Saponification of the top stream may be carried out batch-wise or continuously. The top stream may be subjected to one or more saponification processes. Saponification
reaction temperatures may be from about 40 °C to about 99 °C. In an embodiment, saponification temperatures may range from about 60 °C to about 95 °C. Mixing of the top stream with the basic water layer may be performed during the saponification reaction. Separation of the top stream from the basic water layer may be performed using known methods. The top stream may be subjected to a water wash after separation to remove any sodium salts present. The top stream may be separated using generally known techniques (e.g., fractional distillation) to produce at least two streams, a crude alcohol product stream and a paraffins and unreacted olefins stream. As used herein, “fractional distillation” refers to the distillation of liquids and subsequent collection of fractions of liquids determined by boiling point. The paraffins and unreacted olefins stream may be recycled, transported to other units for processing, stored on site, transported offsite and/or sold.

In certain embodiments, a crude aliphatic alcohol product stream may contain unwanted by-products (e.g., aldehydes, hemi-acetals). The by-products may be removed by subjecting the crude alcohol product stream to a hydrofinishing treatment step to produce an aliphatic alcohol product stream. “Hydrofinishing,” as used herein, refers to a hydrogenation reaction carried out under relatively mild conditions. Hydrofinishing may be carried out using conventional hydrogenation processes. Conventional hydrogenation processes may include passing the crude alcohol feed together with a flow of hydrogen over a bed of a suitable hydrogenation catalyst. The aliphatic alcohol product stream may include greater than about 50 percent by weight of the produced aliphatic alcohols. In some embodiments, the aliphatic alcohol product stream may include greater than 80 percent by weight of the produced aliphatic alcohols. In other embodiments, the aliphatic alcohol product stream may include greater than 95 percent by weight of the produced aliphatic alcohols. The aliphatic alcohol product stream may include branched aliphatic primary alcohols. The resulting aliphatic alcohols in the aliphatic alcohol product stream may be sold commercially, transported off-site, stored on site and/or used in other processing units via product conduit 150.

The composition of an aliphatic alcohol product stream may include hydrocarbons with an average carbon number ranging from 8 to 19. In an embodiment, an average carbon number of the hydrocarbons in aliphatic alcohol product stream may range from 10 to 17. In certain embodiments, an average carbon number of the feed stream may range from 10 to 13. In other embodiments, an average carbon number of the feed stream may
range from 14 to 17. The aliphatic alcohol product stream may include branched primary alcohols. The branched primary alcohol product may be suitable for the manufacture of anionic, nonionic and cationic surfactants. In some embodiments, branched primary alcohol products may be used as the precursor for the manufacture of anionic sulfates, including aliphatic sulfates and oxyalkyl sulfates and oxyalkyl alcohols.

Aliphatic alcohols may have slightly higher aliphatic branching and slightly higher number of quaternary carbons as the olefin precursor. In some embodiments, aliphatic branching may include methyl and/or ethyl branches. In other embodiments, aliphatic branching may include methyl, ethyl and higher aliphatic branching. In certain embodiments, a number of quaternary carbon atoms in the aliphatic alcohol product may be less than 0.5 percent. In other embodiments, a number of quaternary carbon atoms in the aliphatic alcohol product may be less than 0.3 percent. Branching of the alcohol product may be determined by $^1$H NMR analysis. The number of quaternary carbon atoms may be determined by $^{13}$C NMR. A $^{13}$C NMR method for determining quaternary carbon atoms for branched aliphatic alcohols is described in U.S. Patent No. 6,150,322 to Singleton et al., entitled, “Highly Branched Primary Alcohol Compositions and Biodegradable Detergents Made Therefrom.”

In certain embodiments, at least a portion of the paraffins and unreacted olefins stream may exit separator 144 and be recycled, combined with other process streams, sent to other processing units and/or be stored on site via tenth conduit 152. In certain embodiments, a paraffins and unreacted olefins stream may be further separated into a hydrocarbons stream including paraffins and unreacted olefins with a carbon number less than 9. The hydrocarbon stream including paraffins and unreacted olefins with a carbon number less than 9 may be introduced upstream of and/or into the dimerization unit.

Aliphatic alcohols may be converted to oxy alcohols, sulfates or other commercial products. At least a portion of the aliphatic alcohols in the alcohol product stream may be reacted in an oxyalkylation unit with an epoxide (e.g., ethylene oxide, propylene oxide, butylene oxide) in the presence of a base to produce an oxyalkyl alcohol. Condensation of an alcohol with an epoxide allows the alcohol functionality to be expanded by one or more oxy groups. The number of oxy groups may range from 3 to 12. For example, reaction of an alcohol with ethylene oxide may produce alcohol products having between 3 to 12 ethoxy groups. Reaction of an alcohol with ethylene oxide and propylene oxide may
produce alcohols with an ethoxy/propano ratio of ethoxy to propoxy groups from about 4:1 to about 12:1. In some embodiments, a substantial proportion of alcohol moieties may become combined with more than three ethylene oxide moieties. In other embodiments, an approximately equal proportion may be combined with less than three ethylene oxide moieties. In a typical oxyalkylation product mixture, a minor proportion of unreacted alcohol may be present in the product mixture. In an embodiment, at least a portion of the aliphatic alcohol product stream may be formed by condensing a C₅ to C₃₁ aliphatic alcohol with an epoxide. In certain embodiments, a C₅ to C₁₅ branched primary alcohol may be condensed with ethylene oxide and/or propylene oxide. In other embodiments, a C₁₁ to C₁₇ branched primary alcohol may be condensed with ethylene oxide and/or propylene oxide. The resulting oxyalkyl alcohols may be sold commercially, transported off-site, stored on site and/or used in other processing units. In some embodiments, an oxyalkyl alcohol may be sulfated to form an anionic surfactant.

In an embodiment, at least a portion of the alcohols in the aliphatic alcohol product stream may be added to a base. The base may be an alkali metal or alkaline earth metal hydroxide (e.g., sodium hydroxide or potassium hydroxide). The base may act as a catalyst for the oxyalkylation reaction. An amount from about 0.1 percent by weight to about 0.6 percent by weight of a base, based on the total weight of alcohol, may be used for oxyalkylation of an alcohol. In an embodiment, a weight percent of a base may range from about 0.1 percent by weight to 0.4 percent by weight based on the total alcohol amount. The reaction of the alcohol with the base may result in formation of an alkoxide. The resulting alkoxide may be dried to remove any water present. The dried alkoxide may be reacted with an epoxide. An amount of epoxide used may be from about 1 mole to about 12 moles of epoxide per mole of alkoxide. A resulting alkoxide-epoxide mixture may be allowed to react until the epoxide is consumed. A decrease in overall reaction pressure may indicate that the reaction is complete.

Reaction temperatures in an oxyalkylation unit may range from about 120 °C to about 220 °C. In an embodiment, reaction temperatures may range from about 140 °C to about 160 °C. Reaction pressures may be achieved by introducing to the reaction vessel the required amount of epoxide. Epoxides have a high vapor pressure at the desired reaction temperature. For consideration of process safety, the partial pressure of the epoxide reactant may be limited, for example, to less than about 4 atmospheres (413 kPa).
safety measures may include diluting the reactant with an inert gas such as nitrogen. For example, inert gas dilution may result in a vapor phase concentration of reactant of about 50 percent or less. In some embodiments, an alcohol-epoxide reaction may be safely accomplished at a greater epoxide concentration, a greater total pressure and a greater partial pressure of epoxide if suitable, generally known, safety precautions are taken to manage the risks of explosion. With respect to ethylene oxide, a total pressure from about 3 atmospheres (304 kPa) to about 7 atmospheres (709 kPa) may be used. Total pressures of ethylene oxide from about 1 atmosphere (101 kPa) to about 4 atmospheres (415 kPa) may be used in certain embodiments. In an embodiment, total pressures from about 1.5 atmospheres (150 kPa) to about 3 atmospheres (304 kPa) with respect to ethylene oxide may be used. The pressure may serve as a measure of the degree of the reaction. The reaction may be considered substantially complete when the pressure no longer decreases with time.

Aliphatic alcohols and oxyalkyl alcohols may be derivatized to form compositions (e.g., sulphonates, sulfates, phosphates) useful in commercial product formulations (e.g., detergents, surfactants, oil additives, lubricating oil formulations). For example, alcohols may be sulfurized with SO\textsubscript{3} to produce sulfates. The term “sulfurized” refers to a sulfur atom or sulfur containing functionality being added to a carbon or oxygen. Sulfurization processes are described in U.S. Patent No. 6,462,215 to Jacobson et al., entitled “Sulfonation, Sulfation and Sulfamation”; U.S. Patent No. 6,448,435 to Jacobson et al., entitled “Sulfonation, Sulfation and Sulfamation”; U.S. Patent No. 3,462,525 to Levinsky et al., entitled, “Dental Compositions Comprising Long-Chain Olefin Sulphonates;” U.S. Pat. No. 3,428,654 to Rubinfeld et al., entitled, “Alkene Sulphonation Process and Products;” U.S. Patent No. 3,420,875 to DiSalvo et al., entitled, “Olefin Sulphonates;” U.S. Patent No. 3,506,580 to Rubinfeld et al., entitled, “Heat-Treatment Of Sulphonated Olefin Products;” and U.S. Patent No. 3,579,537 to Rubinfeld, entitled, “Process For Separation Of Sulftones From Alkene Sulphonic Acids.”

A general class of aliphatic alcohol sulfates may be characterized by the chemical formula: \((R-O-(A)_x-SO_2)_nM\). \(R'\) represents the aliphatic moiety. “A” represents a moiety of an alkylene oxide; \(x\) represents the average number of \(A\) moieties per \(R-O\) moiety and may range from 0 to 15; and \(n\) is a number depending on the valence of cation \(M\). Examples of cation \(M\) include, but are not limited to, alkali metal ions, alkaline earth metal
ions, ammonium ions and/or mixtures thereof. Examples of cations include, but are not limited to, magnesium, potassium, monoethanol amine, diethanol amine or triethanol amine.

Aliphatic and oxyalkyl alcohols may be sulfated in a sulfation unit. Sulfation procedures may include the reaction of sulfur trioxide (SO₃), chlorosulfonic acid (ClSO₂H), sulfamic acid (NH₂SO₃H) or sulfuric acid with an alcohol. In an embodiment, sulfur trioxide in concentrated (e.g., fuming) sulfuric acid may be used to sulfate alcohols. The concentrated sulfuric acid may have a concentration of about 75 percent by weight to about 100 percent by weight in water. In an embodiment, concentrated sulfuric acid may have a concentration of about 85 percent by weight to about 98 percent by weight in water. The amount of sulfur trioxide may range from about 0.3 mole to about 1.3 moles of sulfur trioxide per mole of alcohol. In certain embodiments, an amount of sulfur trioxide may range from about 0.4 moles to about 1.0 moles of sulfur trioxide per mole of alcohol.

In an embodiment, a sulfur trioxide sulfation procedure may include contacting a liquid alcohol or an oxyalkyl alcohol and gaseous sulfur trioxide in a falling film sulfator to produce a sulfuric acid ester of the alcohol. The reaction zone of the falling film sulfator may be operated at about atmospheric pressure and at a temperature in the range from about 25 °C to about 70 °C. The sulfuric acid ester of the alcohol may exit the falling film sulfator and enter a neutralization reactor. The sulfuric acid ester may be neutralized with an alkali metal solution to form the alkyl sulfate salt or the oxyalkyl sulfate salt. Examples of an alkali metal solution may include solutions of sodium or potassium hydroxide.

The derivatized alcohols may be used in a wide variety of applications. An example of an application includes detergent formulations. Detergent formulations include, but are not limited to, granular laundry detergent formulation, liquid laundry detergent formulations, liquid dishwashing detergent formulations and miscellaneous formulations. Examples of miscellaneous formulations may include general purpose cleaning agents, liquid soaps, shampoos and liquid scouring agents.

Granular laundry detergent formulations may include a number of components besides the derivatized alcohols (e.g., surfactants, builders, co-builders, bleaching agents, bleaching agent activators, foam controlling agents, enzymes, anti-graying agents, optical brighteners and stabilizers). Examples of other surfactants may include ionic, nonionic, amphoteric or cationic surfactants.
Liquid laundry detergent formulations may include the same components as granular laundry detergent formulations. In certain embodiments, liquid laundry detergent formulations may include less of an inorganic builder component than granular laundry detergent formulations. Hydrotropes may be present in the liquid detergent formulations. General purpose cleaning agents may include other surfactants, builders, foam control agents, hydrotropes and solubilizer alcohols.

The formulations may typically include one or more inert components. For example, the balance of liquid detergent formulations may typically be an inert solvent or diluent (e.g., water). Powdered or granular detergent formulations typically contain quantities of inert filler or carrier materials.

EXAMPLES

Example 1. Isomerization of Olefins in a Fischer-Tropsch derived Hydrocarbon Stream. Carbon monoxide and hydrogen were reacted under Fischer-Tropsch process conditions to yield a hydrocarbon mixture of linear paraffins, linear olefins, a minor amount of dienes and a minor amount of oxygenates. The Fischer-Tropsch hydrocarbon stream was separated into different hydrocarbon streams using fractional distillation techniques. A hydrocarbon stream containing olefins and paraffins with an average number of carbon atoms from 8 to 10 was obtained. The composition of the resulting C₈-C₁₀ hydrocarbon stream was analysed by gas chromatography and is tabulated in Table 1.

<table>
<thead>
<tr>
<th>Fischer-Tropsch Hydrocarbon Stream Composition</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₇ and lighter hydrocarbons</td>
<td>0.12</td>
</tr>
<tr>
<td>C₈ branched olefins</td>
<td>0.02</td>
</tr>
<tr>
<td>C₉ linear olefins</td>
<td>0.75</td>
</tr>
<tr>
<td>1-Octene</td>
<td>0.69</td>
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<tr>
<td>n-Octane</td>
<td>2.21</td>
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<tr>
<td>C₉ branched olefins</td>
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<tr>
<td>C₁₀ linear olefins</td>
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</tr>
<tr>
<td>1-Nonene</td>
<td>8.07</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>20.03</td>
</tr>
<tr>
<td>C₁₀ branched olefins</td>
<td>0.28</td>
</tr>
<tr>
<td>C₁₀ linear olefins</td>
<td>22.92</td>
</tr>
<tr>
<td>1-Decene</td>
<td>20.87</td>
</tr>
<tr>
<td>n-Decane</td>
<td>41.12</td>
</tr>
</tbody>
</table>

Table 1
Fischer-Tropsch Hydrocarbon Stream Composition | Wt.%
---|---
C_{11} and heavier hydrocarbons | 0.21
C_9-C_{11} alcohols | 3.56

A zeolite catalyst used for isomerization of linear olefins in the hydrocarbon stream was prepared in the following manner. Ammonium-ferrierite (645 grams) exhibiting a 5.4% loss on ignition and exhibiting the following properties: molar silica to alumina ratio of 62:1, surface area of 369 square meters per gram (P/P_o=0.03), soda content of 480 ppm and n-hexane sorption capacity of 7.3 g per 100 g of ammonium-ferrierite was loaded into a Lancaster mix muller. CATAPAL® D alumina (91 grams) exhibiting a loss on ignition of 25.7% was added to the muller. During a five-minute mulling period, 152 milliliters of deionized water was added to the alumina/ammonium-ferrierite mixture. Next, a mixture of 6.8 grams glacial acetic acid, 7.0 grams of citric acid and 152 milliliters of deionized water was slowly added to the alumina/ammonium-ferrierite mixture in the muller to peptize the alumina. The resulting alumina/ammonium-ferrierite/acid mixture was mulled for 10 minutes. Over a period of 15 minutes, a mixture of 0.20 grams of tetraamine palladium nitrate in 153 grams of deionized water was slowly added to mulled alumina/ammonium-ferrierite/acid mixture. The resulting mixture exhibited a 90:10 ratio of zeolite to alumina and a loss on ignition of 43.5%. The zeolite/alumina mixture was shaped by extruding the mixture through a stainless steel die plate (1/16” holes) of a 2.25 inch Bonnot extruder.

The moist zeolite/alumina extrudate was dried at 125°C for 16 hours. After drying, the zeolite/alumina extrudate was longsbroken manually. The zeolite/alumina extrudate was calcined in flowing air at 200°C for two hours. The temperature was raised to a maximum temperature of 500°C and the zeolite/alumina extrudate was calcined for an additional two hours to yield an isomerization catalyst. The isomerization catalyst was allowed to cool in a desiccator under a nitrogen atmosphere.

Stainless steel tubing, 1 inch OD, 0.6 inch ID and 26 inches long, was used as an isomerization reactor. A thermowell extended 20 inches from the top of the stainless steel reactor tube. To load the reactor tube, the reactor tube was inverted and a piece of glass wool was transferred down the wall of the reactor tube, over the thermowell and positioned at the bottom of the reactor tube to serve as a plug for the reactor tube. Silicon carbide (20 mesh) was added to a depth of about 6 inches to the reactor tube. A second piece of glass
wool was placed over the silicon carbide. A mixture of 6.0 grams of the isomerization catalyst particles (6-20 mesh) and 45 grams of fresh silicon carbide (60-80 mesh) was added to the reactor tube in two parts. The two-part addition distributed the isomerization catalyst evenly in the reactor tube and resulted in an isomerization catalyst bed of about 10 inches in length. A third piece of glass wool was added to the top of the catalyst in the reactor tube. Silicon carbide (20 mesh) was layered onto the third piece of glass wool. A fourth piece of glass wool was positioned over the silicon carbide to serve as a plug for the bottom of the reactor tube. To monitor the temperature of the reaction at various points in the reactor tube, a multipoint thermocouple was inserted into the thermowell of the reactor tube. The temperature above, below and at three different places in the catalyst bed was monitored. The reactor tube was inverted and installed in the furnace. The reactor tube was heated to the operating temperature of 280 °C over a four-hour period under flowing nitrogen. Once the temperature of 280 °C was obtained, the reactor tube was held at the operating temperature for an additional two hours to condition the isomerization catalyst.

After conditioning the isomerization catalyst, the hydrocarbon stream was pumped through the reactor tube at a flow rate of 60 g/hr. Nitrogen, at a flow rate of 6 L/hr, was passed over the isomerization catalyst simultaneously with the hydrocarbon stream. The hydrocarbon stream was vaporized before contacting the isomerization catalyst. The reactor tube was operated at an outlet pressure of 20 kPa above atmospheric pressure.

In Table 2, the weight percent of C₈-C₁₀ branched olefins, C₈-C₁₀ linear olefins and C₈-C₁₀ paraffins in the hydrocarbon stream at 0 hours and in the reactor tube effluent after 24 and 48 hours of isomerization is tabulated. Greater than 90% of the linear olefins in the hydrocarbon stream were converted into branched olefins in the isomerization reactor. During the isomerization step, a small amount of material boiling below C₈ was generated from cracking side reactions. In addition, a portion of the C₉-C₁₁ alcohols present in the feed was dehydrated to yield additional olefins in the product. The average number of alkyl branches on the C₈-C₁₀ olefins in the product was found to be 1.0 as determined by ¹H NMR analysis.
Table 2

<table>
<thead>
<tr>
<th>Fischer-Tropsch Hydrocarbon Stream Composition During Isomerization Reaction</th>
<th>0 Hr Wt.%</th>
<th>24 Hr Wt.%</th>
<th>48 Hr Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈-C₁₀ branched olefins</td>
<td>0.46</td>
<td>33.04</td>
<td>33.16</td>
</tr>
<tr>
<td>C₈-C₁₀ linear olefins</td>
<td>32.19</td>
<td>2.52</td>
<td>2.54</td>
</tr>
<tr>
<td>C₈-C₁₀ paraffins</td>
<td>63.19</td>
<td>63.32</td>
<td>63.27</td>
</tr>
<tr>
<td>Branched to linear C₈-C₁₀ olefin ratio</td>
<td>0.1</td>
<td>13.1</td>
<td>13.1</td>
</tr>
</tbody>
</table>

**Example 2. Isomerization of 1-Dodecene.** 1-Dodecene was obtained from Shell Chemical Co. The composition of 1-dodecene, as assayed by gas chromatography, is tabulated in Table 3.

Table 3

<table>
<thead>
<tr>
<th>1-Dodecene Composition</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Dodecene</td>
<td>98.0</td>
</tr>
<tr>
<td>Other C₁₀-C₁₄ olefins</td>
<td>1.2</td>
</tr>
<tr>
<td>&lt;C₁₀ hydrocarbons</td>
<td>0.2</td>
</tr>
<tr>
<td>&gt;C₁₄ hydrocarbons</td>
<td>0.2</td>
</tr>
<tr>
<td>Paraffins</td>
<td>0.4</td>
</tr>
<tr>
<td>Total C₁₀-C₁₄ hydrocarbons</td>
<td>99.6</td>
</tr>
</tbody>
</table>

1-dodecene was isomerized using the same reactor tube design and isomerization catalyst preparation as described in Example 1. A stream of 1-dodecene was pumped through a reactor tube at a flow rate of 90 g/hr. Nitrogen, at a flow rate of 6 L/hr, was passed over the isomerization catalyst simultaneously with the stream of 1-dodecene. The stream of 1-dodecene was vaporised before contacting the isomerization catalyst. The reactor tube was operated at an outlet pressure of 20 kPa above atmospheric pressure and a temperature of 290°C.

Table 4 is a tabulation of the weight percent of less than C₁₀, C₁₀-C₁₄ and greater than C₁₄ molecules in 1-dodecene at 0 hours and the reactor tube effluent after 168 and 849 hours. Linear C₁₀-C₁₄ olefins were converted in a 94% yield to branched C₁₀-C₁₄ olefins after a 168 hr processing time. During the isomerization step, less than 3 weight percent of material boiling below C₁₀ was generated from cracking side reactions. The average number of alkyl branches on the C₁₀-C₁₄ olefins in the product was determined to be 1.3 by ¹H NMR analysis.
Table 4

<table>
<thead>
<tr>
<th>1-Dodecene Stream Composition During Isomerization Reaction</th>
<th>0 Hr Wt.%</th>
<th>168 Hr Wt.%</th>
<th>849 Hr Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;C&lt;sub&gt;10&lt;/sub&gt; hydrocarbons</td>
<td>0.2</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;14&lt;/sub&gt; hydrocarbons</td>
<td>99.6</td>
<td>97.2</td>
<td>97.4</td>
</tr>
<tr>
<td>&gt;C&lt;sub&gt;14&lt;/sub&gt; hydrocarbons</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Branched C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;14&lt;/sub&gt; olefins</td>
<td>0.6</td>
<td>93.2</td>
<td>93.4</td>
</tr>
<tr>
<td>Linear C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;14&lt;/sub&gt; olefins</td>
<td>99.0</td>
<td>2.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Paraffins</td>
<td>1.0</td>
<td>2.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Example 3. Dehydrogenation of Dodecane with Minimal Isomerization: Dodecane was obtained from Aldrich Chemical Company and stored under nitrogen before being processed. The composition of dodecane, as assayed by gas chromatography, is tabulated in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Dodecane Composition</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>99.3</td>
</tr>
<tr>
<td>&lt;C&lt;sub&gt;10&lt;/sub&gt; hydrocarbons</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C&lt;sub&gt;10&lt;/sub&gt;, C&lt;sub&gt;11&lt;/sub&gt;, C&lt;sub&gt;13&lt;/sub&gt; and C&lt;sub&gt;14&lt;/sub&gt; hydrocarbons</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>&gt;C&lt;sub&gt;14&lt;/sub&gt; hydrocarbons</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Other C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;14&lt;/sub&gt; olefins</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

A paraffin dehydrogenation catalyst was prepared according to Example 1 (catalyst A) of U.S. Patent No. 4,430,517 to Imai et al., entitled “Dehydrogenation Process Using A Catalytic Composition.” The resulting catalyst included 0.8 wt.% platinum, 0.5 wt.% tin, 2.7 wt.% tin, 2.7 wt.% potassium and 1.3 wt.% chlorine on a gamma-alumina support. The atomic ratio of potassium to platinum for this catalyst was 16.8.

[0100] The dehydrogenation catalyst was prepared by dissolving substantially pure aluminum pellets in a hydrochloric acid solution. An amount of stannic chloride was added to the resulting solution to provide a final composite containing 0.5 weight % tin and stirred to distribute the tin component evenly throughout the mixture. Hexamethylenetetramine was added to the resulting tin mixture and the resulting tin-amine mixture was dropped into an oil bath in a manner to form spherical particles having an average particle diameter of about 1/16 inch. The spheres were aged, washed with an
ammoniacal solution, dried and calcined to form a spherical gamma-alumina carrier material. The resulting spheres contained about 0.5 weight % tin in the form of tin oxide. More details about the method of preparing the alumina carrier material are disclosed in U.S. Patent No. 2,620,314 to Hoeskstra, entitled, "Spheroidal Alumina."

The tin-alumina composite was contacted with a deionized solution of chloroplatinic acid and hydrochloric acid (2 weight percent based on alumina weight) in a rotary drier for 15 minutes at room temperature. The amount of chloroplatinic acid used was the amount necessary to incorporate 0.8 weight percent platinum into the tin-alumina composite. The solution was then heated and purged with nitrogen to remove water resulting in a platinum-chlorine-tin-alumina composite. The incorporated chlorine was removed by heating the platinum-chlorine-tin-alumina composite to 550 °C and treating the composite with a 50/50 air/80 °C steam mixture at a gas hourly space velocity (GHSV) of 300 hr⁻¹. After treatment with the air/steam mixture, the platinum-tin-alumina composite contained less than 0.1 weight percent chlorine.

The platinum-tin-alumina composite was contacted with a deionized water solution of potassium nitrate. The amount of potassium nitrate used was the amount necessary to incorporate 2.7 weight percent of potassium in the platinum-tin-alumina composite. The water was removed from the platinum-tin-potassium-alumina composite by heating the composite to 100 °C under a purge of dry air (1000 hr⁻¹ GHSV) for 0.5 hour. The temperature was raised to 525 °C and the platinum-tin-potassium alumina composite was treated with a stream of hydrochloric acid (12 cc/hr, 0.9 M HCl) and a stream of 50/50 air/80 °C steam mixture (300 hr⁻¹ GHSV) to incorporate chlorine into the platinum-tin-potassium-alumina composite. The platinum-tin-potassium-chlorine-alumina composite was dried at 525 °C under a purge of dry air (1000 hr⁻¹ GHSV). The resulting catalyst spheres had an average particle diameter of 1/16 inch and were crushed and sized into 6-20 mesh particle before testing.

Stainless steel tubing, 1 inch OD, 0.6 inch ID and 26 inches long, was used as an isomerization reactor. A thermowell extended 20 inches from the top of the stainless steel reactor tube. To load the reactor tube, the reactor tube was inverted and a piece of glass wool was transferred down the wall of the reactor tube, over the thermowell and positioned at the bottom of the reactor tube to serve as a plug for the reactor tube. Silicon carbide (20 mesh) was added to a depth of about 6 inches to the reactor tube. A second piece of glass
wool was placed over the silicon carbide. A mixture of 6.0 grams of platinum-tin on alumina catalyst particles (6-20 mesh) and 45 grams of fresh silicon carbide (60-80 mesh) was added to the reactor tube in two parts. The two-part addition distributed the catalyst evenly in the reactor tube and resulted in a catalyst bed of about 10 inches in length. A third piece of glass wool was added to the top of the catalyst in the reactor tube. Silicon carbide (20 mesh) was layered onto the third piece of glass wool. A fourth piece of glass wool was positioned over the silicon carbide to serve as a plug for the bottom of the reactor tube. To monitor the temperature of the reaction at various points in the reactor tube, a multipoint thermocouple was inserted into the thermowell of the reactor tube. The temperature above, below and at three different places in the catalyst bed was monitored. The reactor tube was inverted and installed in the furnace. The reactor tube was purged with nitrogen. The reactor tube was heated to the operating temperature of 425°C over a four-hour period under flowing nitrogen (250 standard liters per hour). Once the temperature of 425°C was obtained, the reactor tube was held at the operating temperature for an additional two hours. The catalyst was presulfided by flowing a 1% mixture of hydrogen sulfide gas in hydrogen gas at 425 °C for five minutes through the reactor tube. After 5 minutes, the hydrogen sulfide in hydrogen gas flow was switched to a hydrogen gas flow through the reactor tube.

After presulfiding the catalyst, the reactor tube was maintained at 425 °C for eight hours. After eight hours, the reactor tube pressure was increase to 25 psig with hydrogen gas. Dodecane was pumped through the reactor tube at a flow rate of 40 g/hr at a hydrogen flow rate of 125 standard liters per hour. After four hours, the dodecane stream was increased to 80 g/hr. After obtaining a flow rate of 80 g/hr, the reactor tube temperature was raised to 460 °C. The reactor tube was sampled every eight hours after obtaining the operating temperature of 460°C.

After twenty-four hours the weight percent of dodecane was 11.4 weight percent as depicted in Table 6. At a temperature of 479 °C, the conversion of dodecane to olefins was 16 weight percent after twenty-four hours. Of the olefins, formed 84 weight percent were mono olefins, 4.1 weight percent were aromatic compounds and 7.5 weight percent were di-olefins. Of the total amount of olefins formed, 6 percent were branched, as determined by \(^1\)H NMR analysis.
Table 6

<table>
<thead>
<tr>
<th>Test Results</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt.%) after 24 hours on-stream at 460 °C.</td>
<td>11.4</td>
</tr>
<tr>
<td>Temperature required for 16 wt. % conversion</td>
<td>479 °C</td>
</tr>
<tr>
<td>Selectivity to mono olefins at 16 wt. % conversion</td>
<td>84 wt.%</td>
</tr>
<tr>
<td>Selectivity to aromatics at 16 wt. % conversion</td>
<td>4.1 wt.%</td>
</tr>
<tr>
<td>Selectivity to di-olefins at 16 wt. % conversion</td>
<td>7.5 wt.%</td>
</tr>
<tr>
<td>% Branched C₁₂ olefins in total C₁₂ olefins</td>
<td>6</td>
</tr>
</tbody>
</table>

**Example 4. Dimerization of 1-Hexene.** A dimerization catalyst for the
dimerization of a C₆ olefin stream was prepared by the method for Example 1 in U.S.
Patent No. 5,169,824 to Saleh et al., entitled, "Catalyst Comprising Amorphous NiO On Silica/Alumina Support."

An aluminosilicate cogel (100 gram, 87% by weight SiO₂-13% by weight Al₂O₃) was dispersed in distilled water (2000 mL). Aluminosilicate cogel may be obtained from Ineos Silicas, Netherlands BV, as Synclist-13. Nitric acid (65%) was added to the aluminosilicate/water dispersion with stirring until a pH of 2.7 was obtained. The resulting acidic mixture was filtered and the aluminosilicate solid washed with distilled water until the filtrate exhibited a pH of 5.7. The recovered aluminosilicate solid was dispersed again in distilled water and nitric acid (65%) was added until a pH of 2.7 was obtained. The resulting acidic mixture was filtered and the resulting aluminosilicate solid was washed with distilled water until the filtrate exhibited a pH of 5.7. The recovered aluminosilicate solid was dried for 16 hours at 110 °C in an air atmosphere and thereafter calcined at 500 °C for 16 hours under an air atmosphere.

Ni(NO₃)₂·6 H₂O (67.38 gram) was dissolved in distilled water (700 mL) and heated to a temperature of 32 °C to result in a solution having a pH of 5.7. The aluminosilicate solid (35 gram) was added over time to the nickel solution resulting in a nickel/aluminosilicate slurry. The pH of the nickel/aluminosilicate slurry was
approximately 3.9. The nickel/aluminosilicate slurry was neutralized by adding a solution of (NH₄)₂CO₃ (33.69 gram) in distilled water (200 mL) drop wise over 30 minutes until the pH of the slurry was approximately 6.9. The neutral slurry was stirred for 30 minutes at 32 °C and then filtered to obtain a solid. The recovered solid was slurried twice with water to the original volume of the nickel/aluminosilicate slurry, stirred for 5 minutes and then filtered to obtain a solid. The resulting solid was dried at 110 °C for 16 hours in an air atmosphere. Calcination of the solid was performed by heating the solid under an air atmosphere at increasing temperatures. Initially, the solid was heated to 232 °C for 1 hour. The temperature was raised to 371 °C and the solid heated for 2 hours. After 2 hours, the temperature was raised to 592 °C and the solid was heated for 16 hours. The resulting NiO catalyst dispersed on an aluminosilicate support was crushed and carefully sized to slightly greater than 60 mesh before testing.

A 15 mL reactor tube of an autoclave unit was charged with the NiO catalyst (0.335 grams), 1-hexene (3.35 grams), and a gas chromatography standard (0.67 grams linear tetradecane). Autoclave units of the type “Endeavour” from Argonaut Technologies, United Kingdom, were used to perform the dimerization experiments. The gas cap of the reactor tube was flushed with nitrogen and the reactor tube was heated to 160 °C. Once the reaction temperature of 160 °C was obtained, the reaction temperature was maintained for 10 hours and then cooled to room temperature. The reaction mixture was filtered to remove the NiO catalyst and the filtrate was analysed by gas chromatography. The dimerization results are tabulated in Table 7.

<table>
<thead>
<tr>
<th>Test Results.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion of 1-hexene (%)</td>
<td>59</td>
</tr>
<tr>
<td>C₁₂ olefin dimer in reaction mixture (wt%)</td>
<td>22</td>
</tr>
<tr>
<td>% Branched C₁₂ olefins in total C₁₂ olefins</td>
<td>77</td>
</tr>
</tbody>
</table>

**Example 5. Dimerization of Diluted 1-Hexene.** A 15 mL reactor tube of the autoclave unit was charged with the NiO catalyst (0.335 grams) prepared according to the method for


Example 7, 1-hexene (1.675 grams), hexane (1.675 grams) and a gas chromatography standard (0.67 grams linear tetradecane). The gas cap of the reactor tube was flushed with nitrogen and the reactor tube was heated to 160 °C. Once the reaction temperature of 160 °C was obtained, the reaction temperature was maintained for eight hours and then cooled to room temperature. The reaction mixture was filtered to remove the NiO catalyst and the filtrate was analyzed by gas chromatography. The dimerization results are tabulated in Table 8.

<table>
<thead>
<tr>
<th>Test Results</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion of 1-hexene (wt.%)</td>
<td>54</td>
</tr>
<tr>
<td>C\textsubscript{12} olefin dimer in reaction mixture (wt%)</td>
<td>8</td>
</tr>
<tr>
<td>% Branched C\textsubscript{12} olefins in total C\textsubscript{12} olefins</td>
<td>82</td>
</tr>
</tbody>
</table>
CLAIMS

1. A method for the production of aliphatic alcohols comprising:
   introducing a first hydrocarbon stream comprising olefins and paraffins into a
   hydrogenation unit, wherein the hydrogenation unit is configured to hydrogenate at least a
   portion of olefins in the first hydrocarbon stream to paraffins, and wherein at least a portion
   of the unreacted components of the first hydrocarbon stream and at least a portion of the
   hydrogenated olefins form a second hydrocarbon stream;
   introducing the second hydrocarbon stream into a dehydrogenation unit, wherein
   the dehydrogenation unit is configured to dehydrogenate at least a portion of paraffins in
   the second hydrocarbon stream to olefins, and wherein at least a portion of the unreacted
   components of the second hydrocarbon stream and at least a portion of the olefins from the
   dehydrogenation process form a third hydrocarbon stream;
   introducing the third hydrocarbon stream into a dimerization unit, wherein the
   dimerization unit is configured to dimerize at least a portion of the olefins in the third
   hydrocarbon stream to produce dimerized olefins, and wherein at least a portion of the
   unreacted components of the third hydrocarbon stream and the produced dimerized olefins
   form a fourth hydrocarbon stream and wherein at least a portion of the dimerized olefins
   are branched olefins;
   introducing at least a portion of the fourth hydrocarbon stream into a
   hydroformylation unit;
   introducing a fifth hydrocarbon stream into an isomerization unit, wherein the
   isomerization unit is configured to isomerize at least a portion of linear olefins in the fifth
   hydrocarbon stream to branched olefins, and wherein at least a portion of the unreacted
   components of the fifth hydrocarbon stream and the produced branched olefins form a sixth
   hydrocarbon stream; and,
   introducing at least a portion of the sixth hydrocarbon stream into a
   hydroformylation unit, wherein the hydroformylation unit is configured to hydroformylate
   at least a portion of the olefins in the fourth and sixth hydrocarbon stream to produce
   aliphatic alcohols, wherein at least a portion of the produced aliphatic alcohols comprise a
   branched alkyl group.
2. The method of claim 1, wherein the first hydrocarbon stream and/or the fifth hydrocarbon stream is produced from a Fischer-Tropsch process.

3. The method of any one of claims 1 to 2, wherein the first hydrocarbon stream comprises olefins and paraffins having a carbon number of 4 to 9, particularly 5 to 8.

4. The method of any one of claims 1 to 3, wherein the fifth hydrocarbon stream comprises olefins, particularly olefins having a carbon number from 10 to 18.

5. The method of any one of claims 1 to 4, wherein the hydrogenation unit is operated at a temperature range from about 175 °C to about 250 °C.

6. The method of any one of claims 1 to 5, wherein the hydrogenation unit is operated at a hydrogen flow rate between about 250 NL/L/hr and about 5000 NL/L/hr.

7. The method of any one of claims 1 to 6, wherein the hydrogenation unit is operated at a pressure range from about 10 atmospheres to about 50 atmospheres.

8. The method of any one of claims 1 to 7, wherein the dehydrogenation unit is operated at a temperature range from about 300 °C to about 700 °C.

9. The method of any one of claims 1 to 8, wherein the dehydrogenation unit is operated at a pressure range from about 0.01 atmospheres to about 25 atmospheres.

10. The method of any one of claims 1 to 9, wherein a residence time of at least a portion of the second hydrocarbon stream in the dehydrogenation unit is such that the conversion level of the paraffins in the second hydrocarbon stream to olefins is less than about 50 mole percent.

11. The method of any one of claims 1 to 10, wherein the dimerization unit is operated at temperature range from about 120 °C to about 200 °C.

12. The method of any one of claims 1 to 11, wherein the dimerization unit is configured to produce greater than 50 percent of a branched dimer.

13. The method of any one of claims 1 to 12, wherein the hydroformylation unit is configured to produce greater than about 50 percent of aliphatic alcohols.

14. The method of any one of claims 1 to 13, wherein the hydroformylation unit is operated at a reaction temperature range from about 100 °C to about 300 °C.
15. The method of any one of claims 1 to 14, further comprising:

separating the produced dimerized olefins from the fourth hydrocarbon stream to form a produced dimerized olefins stream and a paraffins and unreacted olefins stream, wherein the paraffins and unreacted olefins stream comprises hydrocarbons of a carbon number less than 9; and,

introducing at least a portion of the paraffins and unreacted olefins stream into the dehydrogenation unit.

16. The method of any one of claims 1 to 15, further comprising adjusting a ratio of olefins and paraffins introduced into the hydroformylation unit by adding at least a portion of a seventh hydrocarbon stream into the hydroformylation unit.

17. The method of any one of claims 1 to 16, further comprising adjusting a ratio of olefins and paraffins introduced into the isomerization unit by adding at least a portion of an eighth hydrocarbon stream into the isomerization unit.

18. The method of any one of claims 1 to 17, further comprising:

forming a hydroformylation reaction stream wherein the hydroformylation reaction stream comprises at least a portion of the unreacted components of the fourth hydrocarbon stream and at least a portion of the produced aliphatic alcohols; and,

separating aliphatic alcohols from the hydroformylation reaction stream to produce a paraffins and unreacted olefins stream and an aliphatic alcohol product stream.

19. The method of claim 18, further comprising, separating olefins from the paraffins and unreacted olefins hydrocarbons stream to produce an olefinic stream, wherein the olefins in the olefinic stream have an average carbon number less than 9, and further comprising introducing at least a portion of the olefinic stream into the dehydrogenation unit, wherein introducing the portion of the olefinic stream into dehydrogenation unit comprises combining at least a portion of the olefinic stream with at least a portion of the second hydrocarbon stream to produce a combined stream upstream of the dehydrogenation unit and introducing at least a portion of the combined stream into the dehydrogenation unit.

20. The method of any one of claims 1 to 19, further comprising introducing at least a portion of the produced aliphatic alcohols into a sulfation unit, wherein the sulfation unit is configured to sulfate at least a portion of the aliphatic alcohols to produce aliphatic
sulfates, wherein at least a portion of the aliphatic sulfates produced comprises branched aliphatic sulfates.

21. The method of any one of claims 1 to 20, further comprising introducing at least a portion of the produced aliphatic alcohols into an oxyalkylation unit, wherein the oxyalkylation unit is configured to oxyalkylate at least a portion of the aliphatic alcohols to produce oxyalkyl alcohols, wherein at least a portion of the oxyalkyl alcohols produced comprises branched oxyalkyl alcohols.

22. The method of any one of claims 1 to 20, further comprising: introducing at least a portion of the produced aliphatic alcohols into an oxyalkylation unit, wherein the oxyalkylation unit is configured to oxyalkylate at least a portion of the aliphatic alcohols to produce an oxyalkyl alcohol stream, wherein at least a portion of the oxyalkyl alcohols produced comprises branched oxyalkyl alcohols; and, introducing at least a portion of the oxyalkyl alcohol stream into a sulfation unit, wherein the sulfation unit is configured to sulfate at least a portion of the oxyalkyl alcohols in the oxyalkyl alcohol stream to produce oxyalkyl sulfates, wherein at least a portion of the oxyalkyl sulfates produced comprises branched oxyalkyl sulfates.

23. A system for the production of aliphatic alcohols configured to perform the method according to any one of claims 1 to 22.