

USE OF RECYCLED BYPRODUCTS TO CREATE HYDROGEN FOR USE IN
CONVERSION OF OLEFINS TO JET FUEL

STATEMENT OF PRIORITY

This application claims priority to United States Provisional Patent Application Ser. No.
5 63/502,333, filed on May 15, 2023, the entirety of which is incorporated herein by reference.

FIELD

[0001] The field is related to a process for producing liquid fuel from carbon dioxide and hydrogen. The field may particularly relate to a process for using recycled hydrogen to supplement the hydrogen produced by a hydrogen production unit.

10 BACKGROUND

[0002] The viability of the methanol to jet (MTJ) complex in the marketplace will be dependent in large part on the overall carbon intensity of the overall CO₂ to jet process, of which MTJ is a part. There are additional upstream units, which include an electrolyzer and methanol synthesis. There may also be CO₂ capture.

15 [0003] Renewable fuels generated from methanol will have at least 2 steps of the process that require the addition of hydrogen: the CO₂ hydrogenation to methanol and a hydrogenation unit to generate fuel-grade hydrocarbons from an upstream dimerization and/or oligomerization unit. The additional H₂ may come from hydrocarbons with or without carbon capture involved (gray and blue H₂, respectively) or, most likely, from a renewable
20 energy source (green H₂). The hydrogen will be costly to generate. It is desirable to drive down the cost of the hydrogen needed for renewable fuels.

BRIEF SUMMARY

[0004] A process is provided for providing hydrogen in a process to produce jet fuel from methanol comprising producing a supply of hydrogen from a hydrogen production unit to be
25 sent to one or more vessels within said process and wherein additional supplies of hydrogen are recovered from a recycle stream or recycle streams from one or more reactors or vessels and sent to supplement said first supply of hydrogen. The additional supplies of hydrogen are taken from a reaction in which hydrogen is not fully consumed. The additional supplies of hydrogen may be taken from a purification or hydrogen concentration unit.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 [0005] FIG. 1 is a schematic drawing of a methanol synthesis process in accordance with an exemplary embodiment of a process for producing light olefins of the present disclosure.
- [0006] FIG. 2 is a schematic drawing of a MTO process in accordance with an exemplary embodiment of a process for producing light olefins of the present disclosure.
- [0007] FIG. 3 is a schematic drawing of an olefinic feed preparation process and apparatus of the present disclosure.
- 10 [0008] FIG. 4 is a schematic drawing of the overall process of the present disclosure.
- [0009] FIG. 5 is a schematic drawing of the light olefins fractionation portion of the process of the present disclosure.
- [0010] FIG. 6 is a schematic drawing of the hydrogenation portion of the process of the present disclosure.

15 DEFINITIONS

- [0011] The term “communication” means that fluid flow is operatively permitted between enumerated components, which may be characterized as “fluid communication”.
- [0012] The term “downstream communication” means that at least a portion of fluid flowing to the subject in downstream communication may operatively flow from the object
20 with which it fluidly communicates.
- [0013] The term “upstream communication” means that at least a portion of the fluid flowing from the subject in upstream communication may operatively flow to the object with which it fluidly communicates.
- [0014] The term “direct communication” means that fluid flow from the upstream
25 component enters the downstream component without passing through any other intervening vessel.
- [0015] The term “indirect communication” means that fluid flow from the upstream component enters the downstream component after passing through an intervening vessel.
- [0016] The term “column” means a distillation column or columns for separating one or
30 more components of different volatilities. Unless otherwise indicated, each column includes a

condenser on an overhead of the column to condense and reflux a portion of an overhead stream back to the top of the column and a reboiler at a bottom of the column to vaporize and send a portion of a bottoms stream back to the bottom of the column. Feeds to the columns may be preheated. The top pressure is the pressure of the overhead vapor at the vapor outlet
5 of the column. The bottom temperature is the liquid bottom outlet temperature. Overhead lines and bottoms lines refer to the net lines from the column downstream of any reflux or reboil to the column. Stripping columns may omit a reboiler at a bottom of the column and instead provide heating requirements and separation impetus from a fluidized inert media such as steam. Stripping columns typically feed a top tray and take main product from the
10 bottom.

[0017] As used herein, the term “diesel” means hydrocarbons boiling in the range of an IBP between 125°C (257°F) and 175°C (347°F) or a T5 between 150°C (302°F) and 200°C (392°F) and the “diesel cut point” comprising a T95 between 343°C (650°F) and 399°C (750°F) using the TBP distillation method or a T90 between 280°C (536°F) and 340°C (644°F) using ASTM D-86. The term “green diesel” means diesel comprising hydrocarbons
15 not sourced from fossil fuels.

[0018] As used herein, the term “T5”, “T90” or “T95” means the temperature at which 5 mass percent, 90 mass percent or 95 mass percent, as the case may be, respectively, of the sample boils using ASTM D-86 or TBP.

20 **[0019]** As used herein, the term “end point” (EP) means the temperature at which the sample has all boiled off using ASTM D-7169, ASTM D-86 or TBP, as the case may be.

[0020] As used herein, the term “jet fuel” means hydrocarbons boiling in the range of a T10 between 190°C (374°F) and 215°C (419°F) and an end point of between 290°C (554°F) and 310°C (590°F). The term “green jet fuel” means jet fuel comprising hydrocarbons not
25 sourced from fossil fuels.

[0021] As used herein, the term “predominant” or “predominate” means greater than 50%, suitably greater than 75% and preferably greater than 90%.

[0022] As used herein, the term “a component-rich stream” or “rich stream” means that the rich stream coming out of a vessel has a greater concentration of the component than the
30 feed to the vessel and preferably than all other streams withdrawn from the vessel.

[0023] As used herein, the term “a component-lean stream” or “lean stream” means that the lean stream coming out of a vessel has a smaller concentration of the component than the feed to the vessel and preferably than all other streams withdrawn from the vessel.

5 [0024] As used herein, the term “rich” means greater than 50%, suitably greater than 75% and preferably greater than 90%.

[0025] As used herein, the term “separator” means a vessel which has an inlet and at least an overhead vapor outlet and a bottoms liquid outlet and may also have an aqueous stream outlet from a boot. A flash drum is a type of separator which may be in downstream communication with a separator that may be operated at higher pressure.

10 DETAILED DESCRIPTION

[0026] The process and apparatus described herein is one embodiment of possible configurations. Simpler configurations are contemplated as well as the multiple stage oligomerization step that is described below.

15 [0027] The process and apparatus disclosed involves the production of a liquid fuel from carbon dioxide and hydrogen. The process comprises reacting a mixture of carbon dioxide and hydrogen to produce methanol, carbon monoxide, and water. The methanol is contacted with an MTO catalyst to produce an olefin stream. The olefin stream is oligomerized with an oligomerization catalyst to produce an oligomerized olefin stream comprising jet fuel, diesel fuel, and alkanes. The oligomerized olefin stream is separated into (1) a liquid fuel stream
20 and (2) an alkane stream. A syngas stream is produced comprising carbon oxides and hydrogen by (1) reforming said alkane stream with steam in a steam reforming reactor, an autothermal reforming reactor, or a dry reforming reactor; or (2) partially oxidizing said alkane stream.

[0028] The conversion of methanol to liquid fuel streams such as sustainable aviation fuel
25 (SAF) is very selective, but light and heavy byproducts of the reaction must be disposed of. One way to improve the overall selectivity of the CO₂ to a liquid fuel stream, *e.g.*, jet complex, (and reduce the carbon intensity) is to recycle the heavier hydrocarbons through CO₂-to syngas routes such as reforming (steam reforming, autothermal reforming or dry reforming) or partial oxidation. The resultant syngas can be recycled into the methanol
30 synthesis unit, thereby increasing jet yield of a CO₂ to jet facility.

[0029] Excess oxygen from a hydrolyzer may be introduced in a partial-oxidation reactor to convert the by-products into syngas, which may then be used as a ready feed for the methanol synthesis unit.

[0030] Methane and hydrogen produced by the process can be mixed with CO₂ and reacted without the use of steam. This requires a non-precious metal-based catalyst developed by Linde and BASF. The resulting syngas can be used to make methanol. It may be possible that other light hydrocarbons in small amounts could also be processed this way. The advantage of this pathway is that it creates the syngas without requiring hydrogen from the electrolyzer, which is the most energy intensive part of the CO₂ to jet complex.

[0031] Liquid byproducts from the MTJ complex are mixed with oxygen from the hydrolysis unit and reacted over a catalyst to convert the hydrocarbons to CO. CO₂ can be co-fed to improve overall CO yields. This process is exothermic once a high enough temperature has been reached.

[0032] There are two main alternatives to this approach:

(1) Steam reforming at high temperatures with CO₂ and steam will create a syngas mixture that can be fed directly to methanol synthesis. This is an endothermic process so requires a substantial amount of external heat. (2) Autothermal reforming combines both partial oxidation and steam reforming. Oxygen from the hydrolysis unit, steam, and CO₂ are reacted over a catalyst to produce an appropriate syngas mixture for conversion to methanol.

Methane and hydrogen (and possibly ethane) from MTJ off-gas streams are mixed with CO₂ to form a syngas mixture of H₂ and CO. This is an endothermic process but can act as a heat sink from other exothermic processes.

[0033] A third alternative, dry reforming, may also be employed. Methane and carbon dioxide is reacted over a catalyst in an endothermic process to form a syngas mixture of H₂ and CO.

[0034] The stream exiting the depropanizer in the oligomerization process will be sent to a reactor where it will be converted to syngas via steam reforming, partial oxidation, autothermal reforming, or dry reforming. Syngas will then be sent to the methanol synthesis unit. If partial oxidation or autothermal reforming is selected to produce the syngas, air or oxygen must also be provided, and additional steam could be extracted from the reactor for use elsewhere in the facility. If steam reforming is selected to produce the syngas from ethane/propane, it will also need steam feeds (which could be fully supplied by the Methanol

to Jet process) and energy input (which could be partially supplied by steam from Methanol To Jet process).

Liquid fuel may be produced from carbon dioxide and hydrogen by the following steps:

- (a) reacting a mixture of carbon dioxide and hydrogen to produce methanol, carbon monoxide, and water;
 - (b) contacting the methanol with an MTO catalyst to produce an olefin stream;
 - (c) oligomerizing said olefin stream with an oligomerization catalyst to produce an oligomerized olefin stream comprising jet fuel, diesel fuel, and alkanes;
 - (d) separating the oligomerized olefin stream into (1) a liquid fuel stream and (2) an alkane stream; and
 - (e) producing a syngas stream comprising carbon oxides and hydrogen by
 - (1) reforming said alkane stream with steam in a steam reforming reactor, an autothermal reforming reactor, or a dry reforming reactor; or
 - (2) partially oxidizing the alkane stream.
- 15 **[0035]** The process for production of a liquid fuel from carbon dioxide and hydrogen may also comprise the following steps:
- (a) reacting a mixture of carbon dioxide and hydrogen to produce a crude methanol stream, containing methanol, water, and other contaminants comprising one or more of hydrogen, CO, CO₂, methane, ethanol, and other oxygenated hydrocarbons;
 - (b) purifying the crude methanol stream by means of distillation to remove light contaminants into a first waste gas stream; heavy contaminants and water into a second heavy waste stream; and to produce a refined methanol stream;
 - (c) contacting the refined methanol stream with an MTO catalyst to produce a crude olefin stream containing ethylene, propylene, butylenes, and other contaminants comprising one or more of hydrogen, CO, CO₂, methane, dimethyl ether, ethanol, and other oxygenated hydrocarbons;
 - (d) purifying the crude olefin stream by means of distillation to remove light ends into a third waste gas stream; followed by water absorption to remove heavy oxygenated hydrocarbons and water extraction to remove dimethyl ether into a DME (dimethyl ether) recycle stream; and to produce one or more refined olefin streams;
 - (e) reacting the one or more of the refined olefin streams with one or more oligomerization catalysts using one or more reaction vessels to produce a crude oligomerized

olefin stream comprising oligomerized olefins with carbon lengths between 4 and 24 carbons and contaminants comprising one or more of hydrogen, methane, and alkanes lighter than pentane;

(f) fractionating the crude oligomerized olefin stream by means of distillation to
5 remove hydrogen and light alkanes into (1) a fourth waste gas stream, (2) a light oligomerized olefin recycle stream, and (3) a refined oligomerized olefin stream comprising olefins having carbon lengths between 12 and 24 carbons;

(g) reacting the refined oligomerized olefin stream with hydrogen with a hydrogenation catalyst to saturate the olefins to paraffins to create a crude jet fuel stream;

10 (h) fractionating the crude jet fuel stream by means of distillation to remove excess hydrogen and light hydrocarbons into (1) a fifth waste gas stream, (2) a sixth waste gas stream comprising naphtha, (3) a seventh waste gas stream comprising diesel, and (4) a liquid fuel comprising jet fuel;

(i) producing a recycle syngas stream comprising carbon oxides and hydrogen by

15 (1) reforming one or more of the waste gas streams with steam in a steam reforming process, an autothermal reforming process, or a dry reforming process; or

(2) partially oxidizing one or more of the waste gas streams; and

(j) co-feeding the recycle syngas stream to the methanol synthesis process of step A.

20 **[0036]** One or more of the waste gas streams may also be reacted with oxygen in a partial oxidation reactor to produce a second recycle syngas stream comprising CO and hydrogen.

[0037] The reaction of step (i) may also be carried out by reacting one or more of the waste gas streams with oxygen and steam in an autothermal reactor to produce a third recycle syngas stream comprising CO and hydrogen. The reaction of step (i) may also be
25 carried out by reacting the sixth waste gas stream with steam in a steam reforming process; by reacting the seventh waste gas stream with steam in a steam reforming process; or by partial oxidation and the resulting recycle syngas stream is thermally integrated with the fractionation process of step (j) in order to provide some or all of the energy required for the distillation.

30 **[0038]** The hydrogen for steps (a) and/or (g) may be produced by a water electrolysis unit and/or the oxygen for autothermal reforming may be produced by a water electrolysis unit.

Where the reaction of step (i) is carried out by partial oxidation, the oxygen for partial oxidation may be produced by a water electrolysis unit. Where the reaction of step (i) is carried out with steam in a steam reforming process, the waste gas stream or streams fed to the steam reforming reactor may contain between 10 wt% and 50 wt% propane. The reaction of step (i) may also be carried out using a dry reforming process. The water electrolysis unit (electrolyzer) produces hydrogen and oxygen from water.

Methanol Synthesis with MTO Reactor

[0039] Carbon dioxide is a so-called greenhouse gas which concentration many desire to suppress in the atmosphere. Carbon dioxide may be converted to oxygenates such as methanol or dimethyl ether. Molecular sieves such as microporous crystalline zeolite and non-zeolitic catalysts, particularly silicoaluminophosphates (SAPO), are known to promote the conversion of oxygenates to hydrocarbon mixtures, particularly hydrocarbon mixtures composed largely of light olefins. The highly efficient Methanol to Olefin (MTO) process may convert oxygenates to light olefins which had been typically considered for plastics production. Light olefins produced from the MTO process are highly concentrated in ethylene.

[0040] Methanol is converted into light olefin products in a methanol to olefin (MTO) process. Molecular sieves such as microporous crystalline zeolite and non-zeolitic catalysts, particularly silicoaluminophosphates (SAPO), are known to promote the conversion of oxygenates such as methanol to hydrocarbon mixtures, particularly hydrocarbon mixtures composed largely of light olefins. SAPO catalysts and their formulation are generally taught in US 4,499,327A, US 10,358,394 and US 10,384,986. Light olefins produced from the MTO process are concentrated in ethylene and propylene but include C4-C6 olefins.

[0041] A mixture of carbon dioxide and hydrogen is reacted to produce methanol, carbon monoxide, and water. The resultant methanol is then contacted with an MTO catalyst to produce an olefin stream.

[0042] The methanol stream is charged to an MTO reactor and contacted with an MTO catalyst at MTO reaction conditions to convert methanol to olefins and water. The methanol stream may include methanol, dimethyl ether, ethanol or combinations thereof. The MTO reaction conditions include contact with a SAPO catalyst at a pressure between 2 MPa and 3.8 MPa. The MTO reaction temperature should be between 325 to 450°C. A weight hourly

space velocity ("WHSV") in the MTO reactor is in the range of 2 to 15 hr⁻¹. The MTO catalyst is separated from the product olefin stream after the MTO reaction.

[0043] Turning to FIG. 1 of an integrated process and apparatus 101 for producing light olefins comprises a methanol synthesis section 111 and a methanol purification section 208.

5 As shown in FIG. 1, a syngas stream in line 122 and a hydrogen gas stream in line 124 are passed to the methanol synthesis section 111. Syngas is defined as a gas comprising primarily carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen (H₂). Optionally, syngas may also include methane (CH₄), and small amounts of ethane and propane. Conventional processes for converting carbon components to syngas include steam reforming, partial
10 oxidation, autothermal reforming, and combinations of these processes. In accordance with an embodiment of the present disclosure, the syngas stream in line 122 may be taken from any suitable sources. In accordance with another embodiment of the present disclosure, the hydrogen gas stream in line 124 may be taken from any suitable sources. In an exemplary embodiment, the hydrogen gas stream in line 124 is taken from a pressure swing adsorption
15 (PSA) unit.

[0044] In accordance with an exemplary embodiment, of the present disclosure, the methanol synthesis section 111 comprises a first methanol converter 140 and a second methanol converter 160. The syngas stream in line 122 and the hydrogen gas stream in line 124 are passed to the first methanol converter 140 of the methanol synthesis section 111. In
20 an embodiment, the syngas stream in line 122 and the hydrogen gas stream in line 124 may be combined to provide a combined feed stream 126 which is passed to the first methanol converter 140. However, the syngas stream in line 122 and the hydrogen gas stream in line 124 may be passed separately to the first methanol converter 140. The combined feed stream 126 may be passed to a syngas pressure booster compressor 130 to compress the syngas to a
25 particular pressure to provide a compressed syngas stream in line 132 before passing to the first methanol converter 140. In an exemplary embodiment, the syngas may be compressed to a pressure from 6890 kPa (1000 psia) to 8970 kPa (1300 psia) in the syngas pressure booster compressor 130. The syngas stream may be heated before passing it to the first methanol converter 140. The compressed syngas stream in line 132 may be heat exchanged in a heat
30 exchanger 133 with a first reactor effluent stream in line 144 to provide a heated syngas stream in line 134. The heated syngas stream in line 134 is passed to the first methanol converter 140.

[0045] In the first methanol converter 140 of the methanol synthesis section 111, the syngas is converted to a methanol composition. The methanol synthesis process is accomplished in the presence of a methanol synthesis catalyst. In an exemplary embodiment, the syngas stream in line 122 to the methanol synthesis section 111 has a molar ratio of carbon dioxide to carbon monoxide of between 1:2 and 1:4 and a molar ratio of hydrogen to carbon oxides (CO+CO₂) in the range of from 3:2 to 3:1.

[0046] A suitable methanol synthesis catalyst may be a copper on a zinc oxide and alumina support. Synthesis conditions of the first methanol converter 140 of the methanol synthesis section 111 may include a temperature of 200 to 300°C and a pressure of 3.5 to 10 MPa. Reaction equilibrium typically requires methanol separation and recycle of unreacted reagents to the synthesis reaction to obtain sufficient conversion.

[0047] In accordance with an exemplary embodiment, the first methanol converter 140 may operate at a temperature of 204°C (400°F) to 290°C (550°F). In accordance with another exemplary embodiment, the first methanol converter 140 may operate at a pressure from 6890 kPa (1000 psia) to 8970 kPa (1300 psia).

[0048] The methanol synthesis reaction is highly exothermic. A boiler feed water (BFW) in line 148 is passed to the first methanol converter 140 to generate a steam stream in line 142 withdrawn from the first methanol converter 140. The generation of steam absorbs the exotherm in the methanol synthesis reaction. The steam stream in line 142 is passed to an overhead separator 145 to separate steam in line 146 from a water stream in line 147. The water stream in line 147 is supplemented with a recycled BFW in line 149 to provide the BFW in line 148 for the first methanol converter 140.

[0049] In the first methanol converter 140, the syngas is converted to a methanol composition in a first reactor effluent comprising methanol in line 144. The methanol stream in the first reactor effluent stream in line 144 may include methanol, dimethyl ether, ethanol or combinations thereof. The first reactor effluent in line 144 is heat exchanged in the heat exchanger 133 with the compressed syngas stream in line 132. A heat exchanged first reactor effluent in line 135 may be heated in a heater 131 to provide a heated first reactor effluent stream in line 136. The heated first reactor effluent stream in line 136 may be further heated in a heater 137 to provide a further heated first reactor effluent stream in line 138. The further heated first reactor effluent stream in line 138 is separated in a first gas-liquid separator 150 to provide a first vapor stream in line 152 and a first liquid stream in line 154. The first vapor

stream in line 152 and the first liquid stream in line 154 may be further processed to recover methanol.

[0050] The first vapor stream in line 152 comprises carbon dioxide that has not yet converted to methanol. The first vapor stream in line 152 may be compressed in a first
5 compressor 155. In an embodiment, the first vapor stream in line 152 may be combined with a make-up hydrogen stream in line 153 to provide a combined first vapor stream in line 156. The combined first vapor stream in line 156 is compressed in the first compressor 155 to provide a compressed first vapor stream in line 157 at a pressure from 6890 kPa (1000 psia) to 8970 kPa (1300 psia). In an embodiment, the make-up hydrogen stream in line 153 may
10 be taken from any suitable sources. In accordance with the present disclosure, the make-up hydrogen stream in line 153 may be taken from one or more units of the process 101.

[0051] The compressed first vapor stream in line 157 is heat exchanged with a second reactor effluent stream in the heat exchanger 163 to provide a heat exchanged first vapor stream in line 158 which is passed to the second methanol converter 160. In the second
15 methanol converter 160 of the methanol synthesis section 111, the unconverted carbon dioxide in the syngas is converted to a methanol composition. The methanol synthesis process is accomplished in the presence of a methanol synthesis catalyst. A suitable methanol synthesis catalyst may be a copper on a zinc oxide and alumina support. Synthesis conditions of the second methanol converter 160 of the methanol synthesis section 111 may include a
20 temperature of 200 to 300°C and a pressure of 3.5 to 10 MPa. Reaction equilibrium typically requires methanol separation and recycle of unreacted reagents to the synthesis reaction.

[0052] A boiler feed water (BFW) in line 176 is passed to the second methanol converter 160 to generate a steam stream in line 166 withdrawn from the second methanol converter 160 to manage the exotherm. The steam stream in line 166 is passed to an overhead separator
25 172 to separate steam in line 171 from a water stream in line 173. The water stream in line 173 is supplemented with a recycled BFW in line 174 to provide the BFW in line 176 for the second methanol converter 160.

[0053] In the second methanol converter 160, the first reactor effluent stream is converted to a methanol composition to provide a second reactor effluent stream comprising methanol
30 in line 162. The methanol stream in the second reactor effluent stream in line 162 may include methanol, dimethyl ether, ethanol or combinations thereof. The second reactor effluent stream in line 162 may be withdrawn from a side of the second methanol converter

160. The second reactor effluent stream in line 162 is heat exchanged in the heat exchanger 163 with the compressed first vapor in line 157. A heat exchanged second reactor effluent stream in line 164 may be heated in a heater 165 to provide a heated second reactor effluent stream in line 166a. The heated second reactor effluent stream in line 166a is separated in a
5 second gas-liquid separator 180 to provide a second vapor stream in line 182 and a second liquid stream in line 184. The second vapor stream in line 182 and the second liquid stream in line 184 may be further processed to recover methanol.

[0054] In accordance an exemplary embodiment, the second methanol converter 160 is operated at a temperature of 204°C (400°F) to 290°C (550°F). In accordance with another
10 exemplary embodiment, the second methanol converter 160 is operated at a pressure from 6890 kPa (1000 psia) to 8970 kPa (1300 psia).

[0055] In accordance with the present disclosure, the second vapor stream in line 182 is passed to a PSA unit 185 to separate hydrogen from the second vapor stream in line 182. In an exemplary embodiment, the second vapor stream in line 182 may be separated into a
15 recycle stream in line 153 and a PSA feed stream in line 184a. In another exemplary embodiment, the recycle stream in line 153 may be passed to the first compressor 155 as the make-up hydrogen stream. In an embodiment, the make-up hydrogen stream in line 153 to the first compressor 155 comprises the recycle stream in line 153.

[0056] The PSA feed stream in line 184a is processed in the PSA unit 185. Typically,
20 PSA unit includes a series of multiple adsorber beds containing one or a combination of multiple adsorbents suitable for adsorbing the particular components to be adsorbed therein. These adsorbents include, but are not limited to, activated alumina, silica gel, activated carbon, zeolite molecular sieve type materials, or any combination thereof. The adsorbents are organized in any sequence as required by the adsorption process to adsorb impurities or
25 components. In the PSA unit 185, PSA feed gas flows over the adsorbents and the more readily adsorbable components are adsorbed during the adsorption step. The remaining gas leaves the adsorber bed in the PSA overhead gas stream 186 that is rich in components and impurities. When the adsorbent has reached its adsorption capacity, it is regenerated to prevent a breakthrough of hydrogen into the PSA overhead gas stream 186.

[0057] In the PSA unit 185, hydrogen present in the PSA feed stream in line 184a is
30 separated into a hydrogen rich stream in line 124. As shown, from the PSA unit, a purge stream in line 186 is separated from the hydrogen rich stream in line 124. The purge stream in

line 186 may be used as fuel. In an exemplary embodiment, the hydrogen rich stream in line 187 may be passed to the syngas pressure booster compressor 130 as the hydrogen stream. In an embodiment, the hydrogen stream in line 124 to the syngas pressure booster compressor 130 comprises the hydrogen rich stream in line 187.

- 5 **[0058]** Turning back to the second gas-liquid separator 180, the second liquid stream in line 184 is withdrawn from the bottoms of the second gas-liquid separator 180 and passed to a third gas-liquid separator 190. The first liquid stream in line 154 may also be passed to the second gas-liquid separator 180. In an exemplary embodiment, the second liquid stream in line 184 may be combined with the first liquid stream in line 154 to provide a combined
- 10 liquid stream in line 188 which is passed to the third gas-liquid separator 190. In the third gas-liquid separator 190, the first liquid stream in line 154 and the second liquid stream in line 184 are separated into a third vapor stream in line 192 and a third liquid stream in line 194. The third liquid stream in line 194 comprises crude methanol. Alternately, the third liquid stream in line 194 may be a crude methanol stream. The crude methanol stream may
- 15 comprise at least 100 ppmw of carbon oxide and/or at least 100 ppmw C2+ oxygenates.
- [0059]** The crude methanol comprises methanol, light ends, and heavier alcohols. As used and described herein, the term "crude methanol" or "crude oxygenate feedstock" may comprise methanol, ethanol, water, light ends, and fuel offs. The light ends may include ethers, ketones, aldehydes, and dissolved gases such as hydrogen, methane, carbon oxides,
- 20 and nitrogen. The crude methanol comprises fusel oil. The fusel oil in the crude methanol typically includes higher alcohols and is generally burned as a fuel in the methanol plant. The crude methanol comprising the fusel oil can be passed to the oxygenate conversion unit for the additional production of light olefins. In accordance with the present disclosure, the crude methanol may be passed to the oxygenate conversion unit or the MTO unit for feed.
- 25 **[0060]** In accordance with an exemplary embodiment of the present disclosure, the crude methanol may have a composition comprising carbon monoxide in a concentration from 0 to 1 wt%, carbon dioxide in a concentration from 0.05 wt% to 2 wt%, methane in a concentration from 0.001 wt% to 2 wt%, hydrogen in a concentration from 0.05 wt% to 2 wt%, oxygen in a concentration from 0 to 1 wt%, water in a concentration from 5 wt% to
- 30 18 wt%, nitrogen in a concentration from 0 to 1 wt%, methanol in a concentration from 75 wt% to 90 wt%, and alcohols (other than methanol) in a concentration from 0.05 to 4 wt%.

[0061] The third liquid stream in line 194 may be passed to a crude methanol hold-up tank 195. A crude methanol stream in line 196 is withdrawn from the crude methanol hold-up tank 195. In accordance with the present disclosure, the crude methanol stream in line 196 may be passed to the oxygenate conversion unit 200 as shown in FIG. 1.

5 **[0001]** Conventionally, the crude methanol stream in line 196 is purified of the light gases and heavy oxygenates before it is charged to a MTO reactor 202 in an oxygenate conversion unit 200. In accordance with the embodiment of FIG. 1, the crude methanol stream comprising at least 100 ppmw of carbon oxide and/or at least 100 ppmw C₂+ oxygenates is passed directly to the MTO reactor 202 after it is vaporized in a fired heater.

10 **[0062]** The superheated crude methanol stream in line 199' is charged to the MTO reactor 202 and contacted with an MTO catalyst at MTO reaction conditions to convert methanol and other oxygenates to olefins and water. The crude methanol stream in line 198 may include methanol, dimethyl ether, ethanol or combinations thereof. The MTO reactor 202 may fluidize catalyst at fast fluidized conditions. The MTO catalysts may be a
15 silicoaluminophosphate (SAPO) catalyst. SAPO catalysts and their formulation are generally taught in US 4,499,327A, US 10,358,394 and US 10,384,986. The MTO reaction conditions include contact with a SAPO catalyst at a pressure between 2 MPa and 3.8 MPa. The MTO reaction temperature should be between 325 to 450°C. A weight hourly space velocity ("WHSV") in the MTO reactor 202 is in the range of 2 to 15 hr⁻¹. The MTO catalyst is
20 separated from the product olefin stream after the MTO reaction.

[0063] In the MTO process, catalyst particles are repeatedly circulated between the MTO reactor 202 and the MTO regenerator unit 204. During regeneration, coke deposited on the catalyst particles during reaction in the reaction zone is removed at elevated temperatures by oxidation in the regenerator unit 204. The removal of coke deposits restores the activity of the
25 catalyst particles to the point where they can be reused in the MTO reactor 202. The regenerated catalyst is discharged from the regenerator unit 204 in line 206 and recycled to the MTO reactor 202. A MTO effluent stream of light olefins comprising ethylene and propylene and other olefins along with water and oxygenates are discharged from the MTO reactor 202 in an effluent line 207.

30 **[0064]** In accordance with an exemplary embodiment, the crude methanol stream in line 196 may be passed to the methanol purification section 208 comprising at least two distillation columns, a first distillation column 210 and a second distillation column 220. The

crude methanol stream in line 196 is heat exchanged with a product stream in a heat exchanger 197 to provide a heat exchanged crude methanol stream in line 194 or a heat exchanged third liquid stream in line 198. The heat exchanged crude methanol stream in line 198 may be passed to the first distillation column 210. In the first distillation column 210, the light gas(es) are separated from the crude methanol in a first distillation column overhead stream in line 212. The light gases separated from the crude methanol stream include carbon monoxide, carbon dioxide, methane, hydrogen and dimethyl ether. The first distillation column overhead stream in line 212 is passed to a first overhead receiver 215 where the light gas(es) are separated in a first overhead receiver vapor stream in line 214. The first overhead receiver vapor stream in line 214 may be passed to a fuel section or used as a fuel perhaps in the combustor 254 in line 256 of FIG. 1. From the first overhead receiver 215, an overhead receiver liquid stream is withdrawn in line 216 and passed to a top of the first distillation column 210.

[0065] A first distillation column bottoms stream comprising methanol in line 218 is withdrawn for further separation. The first distillation column bottoms stream in line 218 is separated into a first reboiling stream in line 218b and a first distillation column effluent stream in line 218a. The first reboil stream in line 218b is reboiled in a reboiler 219 before passing to the first distillation column bottom. In accordance with an exemplary embodiment, the first distillation column 210 is operated at a pressure from 689 kPa (100 psia) to 1379 kPa (200 psia). In accordance with another exemplary embodiment, the first distillation column is operated at a temperature of 27°C (80°F) to 177°C (350°F).

[0066] The first distillation column effluent stream in line 218a includes heavy oxygenates such as C2+ alcohols, ketones, aldehydes that should be removed from the crude methanol stream. Hence the first distillation column effluent stream in line 218a is further separated in a second distillation column 220. In the second distillation column 220, the first distillation column effluent stream in line 218a is separated into a second distillation column overhead stream in line 222 comprising methanol and a second distillation column bottoms stream in line 226. The second distillation column overhead is in the vapor phase. Instead of condensing it, a methanol charge stream is taken from the second distillation column overhead line 222 and charged to the MTO reactor 202 in line 199'. A portion of the overhead stream in line 222 may be condensed for reflux to the column in line 228. From the heat exchanger 223, a partially condensed second distillation column overhead stream in line

224 is passed to a second overhead receiver 225. In the second overhead receiver 225, the condensed portion of the second distillation column overhead stream in line 224 is recycled to the second distillation column 220.

[0067] A second distillation column bottoms stream in line 226 is withdrawn from the column. The second distillation column bottoms stream in line 226 is separated into a second reboiling stream in line 226b and a second distillation column effluent stream in line 226a. The second reboiling stream in line 226b is reboiled in a reboiler 230 before passing to the second distillation column bottom section.

[0068] In accordance with an exemplary embodiment, the second distillation column is operating at a pressure from 517 kPa (75 psia) to 862 kPa (125 psia). In accordance with yet an exemplary embodiment, the second distillation column operates at a temperature of 104°C (220°F) to 149°C (300°F). The second distillation column effluent stream in line 226a will comprise heavy oxygenates and water, an aqueous oxygenate stream.

[0069] In the embodiment of FIG. 1, heavy oxygenates in the crude methanol stream will be processed with the MTO effluent stream in line 207 and be separated into an oxygenate rich stream. In accordance with an embodiment of the present disclosure, the methanol purification section 208 may also comprise a third distillation column (not shown) for further removing heavy oxygenates from the crude methanol stream. In accordance with an exemplary embodiment, the third distillation column may operate at a pressure from 106 kPa (15 psia) to 345 kPa (50 psia). In accordance with another exemplary embodiment of the present disclosure, the third distillation column may be an atmospheric column operating at atmospheric pressure. In accordance with yet an exemplary embodiment, the second distillation is operated at a temperature of 48°C (120°F) to 122°C (250°F).

[0070] When a third column is also employed, the second distillation column effluent stream in line 226a is separated in the third distillation column to provide an overhead stream comprising methanol and a bottoms stream. The overhead stream may be passed to the MTO reactor 202 along with the methanol product stream from line 222 in MTO charge line 199'.

Olefinic Feed Preparation

[0071] FIG. 2 shows the olefinic feed preparation process and apparatus of the present disclosure. A process and apparatus 10, a superheated MTO effluent stream of light olefins from effluent line 207 of FIG. 1 is fed via line 12 to an oxygenate conversion reactor 16 that reacts an oxygenate such as methanol or dimethyl ether (DME) with fluidized catalyst. The

hot vaporous reactor effluent stream in line 14 may be preliminarily cooled in a reactor effluent heat exchanger 15 to recover heat before it is passed to a quench tower 20. In the quench tower 20, the vaporous reactor effluent is desuperheated, neutralized of organic acids and clarified of catalyst fines by direct contact with a water stream supplied in line 19 which
5 may be taken from a stripped water stream in line 21. A quenched reactor effluent stream in line 22 is discharged from the quench tower 20 and fed to a product separator column 24. The product separator column 24 may be in downstream communication with the MTO reactor 202 of FIG. 1.

[0072] Product separator 24 comprises two sections for separating the reactor effluent
10 stream into a product olefin stream in an overhead line 40, an intermediate liquid stream in an intermediate line 28 and a water stream in a bottoms line 26. A first, or lower, section receives the quenched reactor effluent stream in line 22. In the lower section, most of the heat is removed from the quenched reactor effluent stream while partially condensing the water in the quenched reactor effluent stream to generate a product water stream in bottoms line 26
15 comprising a portion of the oxygenate byproducts in the quenched reactor effluent stream in line 22. A portion of the product water stream is cooled and pumped around to the top of the first section of the product separator 24 to cool the quenched reactor effluent stream in line 22. A second portion of the second bottoms stream 26 is passed to a water stripper column 30. A water return stream comprising oxygenate byproducts from the compression section 80
20 in return line 32 can also be passed to the water stripper column 30. The water stripper column 30 may be in downstream communication with the product separator column 24.

[0073] A vapor stream from the first section of the product separator 24 is passed to the second, or upper, section of the product separator. An intermediate stream in line 28
25 comprising hydrocarbons, oxygenate byproducts, and water in liquid phase is withdrawn at a bottom of the upper section. A portion of the intermediate stream in line 28 is cooled and passed as reflux to the top of the second section of the product separator 24. The remainder of the intermediate stream in line 28 is passed to a coalescer 29 to separate a hydrocarbon overhead stream from an aqueous stream in line 34 which is fed back to the product water stream and pumped to the water stripper column 30 in line 36. An overhead product stream
30 comprising olefins from the product separator column in line 40 is delivered to the compression section 80.

[0074] The product water stream in line 36 includes dilute hydrocarbon oxygenates such as DME, methanol, acetaldehyde, acetone and MEK (methyl ethyl ketone). The water stripper column 30 separates or strips the oxygenates into a methanol and oxygenate rich stream in an overhead line 49 rich in both methanol and at least another oxygenate and a water rich stream in a bottoms line 46.

[0075] In one embodiment the water stripper column 30 temperature may be at the bottom of the water stripper column and the pressure may be 75 kPa gauge (11 psig) to 345 kPa (50 psig) at the top of the water stripper column.

[0076] The product olefin stream in the product overhead line 40 carries valuable olefinic products which must be recovered. The compression section 80 increases the pressure of the product olefin stream necessary for downstream processing such as used in conventional light olefin recovery units. The compression section 80 may comprise a first knock out drum 82 which separates the product olefin stream into a pressurized first olefin rich stream at a temperature of 40°C (104°F) to 60°C (140°F) and a pressure of 193 kPa (g) (28 psig) to 262 kPa (g) (38 psig) in an overhead line 83 and a first aqueous stream rich in oxygenates in a bottoms line 84. The olefin rich stream in the overhead line 83 may be fed to a compressor 85, cooled and directed to a second knockout drum 86. The aqueous stream in the bottoms line 84 is pumped via a manifold line 76 to the return line 32 which returns the water stream with the product water stream in the separator bottoms line 36 to the water stripper column 30.

[0077] The compression section 80 may comprise a second knock out drum 86 which separates the pressurized first olefin rich stream into a second pressurized olefin rich stream at a pressure of 330 kPa (g) (48 psig) to 400 kPa (g) (58 psig), and a temperature of 27°C (80°F) to 54°C (130°F) in an overhead line 87 and a second aqueous stream rich in oxygenates in a bottoms line 88. The second olefin rich stream in the overhead line 87 may be fed to a compressor 89, cooled and directed to a third knockout drum 90. The aqueous stream in the bottoms line 88 is pumped to the return line 32 via the manifold line 76 which returns the water stream with the product water stream in the separator bottoms line 36 to the water stripper column 30.

[0078] The compression section 80 may comprise a third knock out drum 90 which separates the pressurized second olefin rich stream into a third pressurized olefin rich stream in an overhead line 91 and a third aqueous stream rich in oxygenates in a bottoms line 92.

The third olefin rich stream in the overhead line 91 may be fed to the oxygenate absorber column 50. The aqueous stream in the bottoms line 92 is pumped to the return line 32 via manifold line 76 which returns the water stream with the product water stream in the separator bottoms line 36 to the water stripper column 30.

- 5 **[0079]** Types of suitable compressors may include centrifugal, positive displacement, piston, diaphragm, screw, and the like. In one embodiment, the compressors 85, 89 in the compression section 80 are centrifugal compressors. The final discharge pressure can be between 1 MPa gauge (145 psig) and 2 MPa gauge (290 psig). The compressor discharge may be cooled to ambient temperatures using conventional heat transfer methods.
- 10 **[0080]** As illustrated in the FIG. 2 and according to a preferred embodiment, at least a portion of the compressed product stream via the overhead line 91 is contacted in the oxygenate absorber column 50 at effective conditions to absorb at least a quantity of effluent oxygenates with a cooled lean water stream with no water taken directly from the product separator column 24 without prior removal of oxygenates. The contacting in the oxygenate
- 15 absorber column 50 produces an absorption olefin rich stream in the overhead line 54 and an absorption water rich stream in a bottoms line 52 comprising a quantity of effluent oxygenates. The oxygenate absorber may have operating conditions including a bottoms temperature range of 30°C (86°F) to 60°C (140° F) and an overhead pressure range of 700 kPa gauge (101 psig) to 1 MPa gauge (145 psig).
- 20 **[0081]** The absorption olefin rich stream in the overhead line 54 may be fed to an absorber separator 60 in which a gaseous olefin stream is taken in an overhead line 61 to a third compressor 62 while water and oxygenates are taken in the bottoms line 59 to the manifold line 76. The gaseous olefin stream in line 61 is compressed in the third compressor combined with the stream in line 71 via line 63, partially condensed by cooling in the heat
- 25 exchanger 64 and fed in line 65 to a stripper separator 66. The stripper separator separates an aqueous stream including oxygenates in the boot in line 67 which feeds the manifold line 76, a light olefinic vapor stream in an overhead line 68 comprising C3- olefins and a heavy olefinic liquid stream comprising C4+ olefins in line 69. The heavy olefinic liquid stream in line 69 is stripped in a DME stripper column 70 to remove C3- and lighter vapors in a
- 30 stripper overhead line 71 from the heavy olefinic liquid stream in the stripper bottoms line 168. Most oxygenates will be stripped into the stripper overhead line 71 and be separated after cooling upon recycle to the stripper separator 66. The bottom stream exiting the DME

- stripper column 70 may be sent through line 168 to hydrogenation. This stream comprises mostly C₄⁺ olefins but comprises diolefins that will deter the oligomerization catalyst requiring selective hydrogenation. The stripper separator may operate at a temperature of 30°C (86°F) to 60°C (140°F) and a pressure of 1.7 MPa (g) (250 psig) to 2.1 MPa (g) (300 psig). The light olefinic vapor stream in the overhead line 68 is scrubbed in a caustic scrubber column 73 by countercurrent contact with a caustic solution in line 342 to absorb acid gases such as carbon dioxide from the light olefinic vapor which exits the caustic scrubber 73 in an overhead line 74. The acid gas rich caustic solution exits scrubber 73 in line 44.
- 10 **[0082]** The scrubbed light olefinic vapor in overhead line 74 may be refrigerated by propylene refrigerant in a cryogenic cooler 75 to liquefy part of the light olefinic stream and separated in a drier separator 46a to provide an aqueous stream from a boot which is taken to the manifold line 76 and a vaporous light olefin stream comprising C₂- hydrocarbons and gases in an overhead line 77 and a liquid light olefin stream in a bottoms line 78 comprising
- 15 C₃⁺ hydrocarbons. The vaporous light olefin stream in the overhead line 77 is dried in a drier 79a to provide a vaporous product olefin stream in line 112. The liquid light olefin stream in the bottoms line 78 is dried in a drier 79b to provide a liquid product olefin stream in line 114. The product olefin streams in lines 112 and 114 are processed in the oligomerization feed preparation section.
- 20 Oligomerization
- [0083]** Olefin oligomerization is a process that can oligomerize smaller olefins into larger olefins. More specifically, it can convert olefins including oligomerized olefins into a distillates including jet fuel and diesel range products. The oligomerized distillate can be saturated for use as transportation fuels.
- 25 **[0084]** Jet fuel is one of the few petroleum fuels that cannot be replaced easily by electrical motor systems because a high energy output is required to fuel planes which cannot be supplied with electric motors. Jet fuel has an end point boiling specification of less than 300°C using ASTM D86. Large incentives are currently available for green jet fuel in certain regions.
- 30 **[0085]** The oligomerization section 310 is illustrated in FIG. 3. A charge olefin stream and a recycle olefin stream are oligomerized with a first-stage oligomerization catalyst to produce a first-stage oligomerized olefin stream. The first-stage oligomerized olefin stream

is oligomerized with a second-stage oligomerization catalyst to provide a second-stage oligomerized stream. A dealkanizer column can be used to remove light alkanes that would be inert and accumulate in a recycle loop. The second-stage oligomer product stream is hydrogenated to produce fuels.

5 **[0086]** Turning to the oligomerization section 310 of FIG. 3, a charge olefin stream in line 312 is provided to the oligomerization section 310. The charge olefin stream may comprise substantial ethylene and propylene. The charge olefin stream may predominantly comprise ethylene and/or propylene. In an aspect, the charge olefin stream may comprise at least 95 mol% ethylene and/or propylene. The charge olefin stream in line 312 may be styled
10 a light olefin stream. Additional olefinic species with carbon numbers ranging from C4 to C6 can be expected in the charge stream. The light olefin stream may be provided by the dehydration of ethanol or provided from a MTO unit. The charge olefin stream may be at a temperature of 60°C (140°F) to 150°C (302°F), preferably 80°C (176°F) to 100°C (212°F), and a pressure of 3.5 MPag (500 psig), preferably 5.6 MPag (800 psig) to 8.4 MPag (1200
15 psig).

[0087] The charge olefin stream may be initially contacted with a first-stage oligomerization catalyst to oligomerize the ethylene and propylene to oligomers and then contacted with a second oligomerization catalyst to oligomerize unconverted ethylene and propylene from the first-stage oligomerization. Alternatively, the olefin stream may be
20 initially contacted with a second stage oligomerization catalyst to oligomerize ethylene and propylene, and then be contacted with the first-stage oligomerization catalyst to oligomerize the oligomerized ethylene and propylene.

[0088] The oligomerization reaction generates a large exotherm. For example, dimerization of ethylene can generate 612 kcal/kg (1100 BTU/lb) of heat. Consequently,
25 this large exotherm must be managed. Accordingly, the charge olefin stream in line 312 may be split into multiple olefin streams. In FIG. 3, the charge olefin stream is split into two separate streams: a first charge olefin stream in a first charge olefin line 312a and a second charge olefin stream in a second charge olefin line 312b. More or less separate multiple olefin streams may be used. Up to six charge olefin streams are readily contemplated. The
30 charge olefin stream in line 312 may be split into equal aliquot multiple olefin streams. Alternatively, the charge olefin stream in line 312 may be split into unequal streams. For example, the charge olefin stream may be split into streams of descending flow rates in which

a charge olefin stream to a preceding reactor has a larger flow rate than a charge olefin stream to a subsequent reactor. In an embodiment, the charge olefin stream is split into two streams of equal flow rates, each comprising 50 vol% of the charge olefin stream. In another embodiment, the first charge olefin stream in the first charge olefin line 312a may comprise
5 70 to 90 vol% of the charge olefin stream and the second charge olefin stream in the second olefin line 312b may comprise 10 to 30 vol% of the charge olefin stream.

[0089] To manage the exotherm, the charge olefin stream may be diluted with a diluent stream to provide a diluted olefin stream to absorb the exotherm. The diluent stream may comprise a paraffin stream in a diluent line 314. The diluent stream in the diluent line 314
10 may be added to the first charge olefin stream in the first charge olefin line 312a before it is charged to the first-stage oligomerization reactor 322. Preferably, the diluent stream is added to the first charge olefin stream in line 312a after the split of the charge olefin stream in line 312 into multiple olefin streams to provide a first diluted olefin charge stream in line 316a, so the diluent stream passes through all of the first-stage oligomerization reactions.
15 Alternatively, the diluent stream may also be split into multiple streams with each diluent stream added to a corresponding charge olefin stream. The diluent stream may have a volumetric flow rate of 2 to 8 times and preferably 3 to 6 times the volumetric flow rate of the charge olefin stream in the charge olefin line 312.

[0090] A recycle olefin stream in a recycle line 326 comprising C4 to C8 olefins may be
20 mixed with the charge olefin stream and oligomerized in the first-stage oligomerization reactor 322. In an embodiment, the recycle olefin stream in line 326 is split into a plurality of recycle olefin streams 326a-326d. A recycle olefin stream in a first recycle olefin line 326a may be mixed with the first charge olefins stream in line 312a and charged to the first-stage oligomerization reactor 322. In a further embodiment, the first recycle olefin stream in the
25 first recycle olefin line 326a is mixed with the first charge olefin stream in line 312a and the diluent stream in line 314 to provide a diluted first charge olefin stream in line 316a.

[0091] The first diluted charge olefin stream may comprise no more than 35 wt% olefins, suitably no more than 30 wt% olefins and preferably no more than 20 wt% olefins. In an embodiment, the first diluted olefin stream comprises 10 to 30 wt% C2 to C8 olefins. The
30 first diluted olefin stream may comprise no more than 30 wt% ethylene, suitably no more than 25 wt% ethylene and preferably no more than 20 wt% ethylene. In an embodiment, the first diluted charge olefin stream comprises 10 to 20 wt% propylene. The first diluted charge

olefin stream may comprise no more than 30 wt% propylene, suitably no more than 25 wt% propylene and preferably no more than 20 wt% propylene. In an embodiment, the first diluted charge olefin stream comprises 10 to 20 wt% propylene.

[0092] The first-stage oligomerization reactor 322 may comprise a series of first-stage oligomerization catalyst beds 322a, 322b, 322c and 322d each for charging with an olefin charge stream 312a, 312b, 312c, and 312d, respectively. The first-stage oligomerization reactor preferably contains four fixed first-stage oligomerization catalyst beds 322a, 322b, 322c and 322d. It is also contemplated that each first-stage oligomerization catalyst bed 322a, 322b, 322c and 322d may be in a dedicated first-stage oligomerization reactor or multiple first-stage oligomerization catalyst beds may be in two or more separate first-stage oligomerization reactor vessels. Up to six, first-stage oligomerization catalyst beds are readily contemplated. In FIG. 3, two, first stage oligomerization reactor vessels 321a and 321b are utilized.

[0093] A parallel first-stage oligomerization reactor may be used when the first-stage oligomerization reactor 322 has deactivated during which the first-stage oligomerization reactor 322 is regenerated in situ by combustion of coke from the catalyst. In another embodiment, each first-stage oligomerization reactor may comprise a lead reactor, a lag reactor and a spare reactor to facilitate regeneration. Only two reactor vessels 321a, 321b are shown in FIG. 3.

[0094] The diluted first charge olefin stream in line 316a may be cooled in a first charge cooler 318a to provide a cooled diluted first charge olefin stream in line 320a and charged to a first bed 322a of first-stage oligomerization catalyst in the first, first-stage oligomerization reactor vessel 321a of the first-stage oligomerization reactor 322. The cooled diluted first charge olefin stream in line 320a may be charged at a temperature of 180°C (356°F) to 260°C (500°F) and a pressure of 3.5 MPag (500 psig) to 8.4 MPag (1200 psig). The charge cooler 318a may comprise a steam generator.

[0095] The diluted first charge olefin stream may be charged to the first, first-stage catalyst bed 322a in line 320a preferably in a down flow operation. However, upflow operation may be suitable. As oligomerization of ethylene, propylene and recycle olefins occurs in the first, first-stage oligomerization catalyst bed 322a, an exotherm is generated due to the highly exothermic nature of the olefin oligomerization reaction. Oligomerization of the first charge olefin stream produces a first oligomerized effluent stream in a first oligomerized

effluent line 324a at an elevated outlet temperature despite the cooling and dilution. The elevated outlet temperature is limited to between 150°C (302°F) and 250°C (482°F).

- [0096]** The second charge olefin stream in line 312b may be mixed with a second recycle olefin stream in a second recycle olefin line 326b and with the first oligomerized effluent stream in the first oligomerized effluent line 324a removed from the first, first-stage oligomerization catalyst bed 322a in the first, first-stage reactor 321a to provide a mixed second charge olefin stream in line 316b. The first oligomerized effluent stream in line 324a includes the diluent stream from diluent line 314 added to the first olefin charge stream in line 312a. The second charge olefin stream may comprise no more than 35 wt% C2 to C8 olefins, suitably no more than 25 wt% C2 to C8 olefins and preferably no more than 20 wt% ethylene. The second charge olefin stream may comprise no more than 30 wt% ethylene, suitably no more than 25 wt% ethylene and preferably no more than 20 wt% ethylene. The second charge olefin stream may comprise no more than 30 wt% propylene, suitably no more than 25 wt% propylene and preferably no more than 20 wt% propylene. The second charge olefin stream in line 316b may be cooled in a second charge cooler 318b which may be located externally to the first, first-stage oligomerization reactor 321a to provide a cooled second charge olefin stream in line 320b and charged to a second bed 322b of first-stage oligomerization catalyst in the first, first-stage oligomerization reactor 321a. The charge cooler 318b may comprise a steam generator.
- [0097]** The second charge olefin stream in line 320b may be charged at a temperature of 180°C (356°F) to 230°C (446°F) and a pressure of 3.5 MPag (500 psig) to 8.4 MPag (1200 psig). The second charge olefin stream will include diluent and olefins from the first oligomerized stream. The olefins from the first oligomerized stream will oligomerize in the second catalyst bed 322b. Oligomerization of ethylene, propylene, recycle olefins and oligomers in the second olefin stream in the second bed 322b of first-stage oligomerization catalyst produces a second oligomerized olefin effluent stream in a second oligomerized effluent line 324b at an elevated outlet temperature. The elevated outlet temperature may be limited to between 30°C (54°F) and 50°C (90°F) above the inlet temperature to the catalyst bed 322b.
- [0098]** The second oligomerized effluent stream in line 324b removed from the second, first-stage oligomerization catalyst bed 322b in the first, first-stage reactor vessel 321a may be mixed with a third recycle olefin stream in a third recycle olefin line 326c to provide a first

recycle olefin charge stream in line 316c. None of the charge olefin stream in line 312 is directly added to the first recycle olefin charge stream in line 316c. Alternatively, a portion of the charge olefin stream in line 312 may be charged with the second oligomerized effluent stream with the first recycle olefin charge stream in line 316c. The second oligomerized effluent stream in line 324b includes the diluent stream from diluent line 314 added to the first charge olefin stream in line 312a. The first recycle olefin charge stream may comprise no more than 30 wt% ethylene, suitably no more than 25 wt% ethylene and preferably no more than 20 wt% ethylene. The first recycle olefin charge stream may comprise no more than 30 wt% propylene, suitably no more than 25 wt% propylene and preferably no more than 20 wt% propylene. The first recycle olefin charge stream may comprise no more than 30 wt% C2 to C8 olefins, suitably no more than 25 wt% C2 to C8 olefins and preferably no more than 20 wt% C2 to C8 olefins. The first recycle olefin charge stream in line 316c may be cooled in a third charge cooler 318c which may be located externally to the oligomerization reactor 322 to provide a cooled first recycle olefin charge stream in line 320c and charged to a third bed 322c of first-stage oligomerization catalyst in the first-stage oligomerization reactor 322. In an embodiment, the third bed 322c of first-stage oligomerization catalyst is provided in a second, first-stage oligomerization reactor vessel 321b. The charge cooler 318c may comprise a steam generator.

[0099] The cooled first recycle olefin charge stream in line 320c may be charged at a temperature of 180°C (356°F) to 230°C (446°F) and a pressure of 3.5 MPag (500 psig) to 8.4 MPag (1200 psig). The first recycle olefin charge stream will include diluent and olefins from the second oligomerized olefin stream and the third recycle olefin stream. The olefins will oligomerize in the third catalyst bed 322c. Oligomerization of ethylene and propylene and oligomerization of oligomers in the first recycle olefin charge stream in the third bed 322c of first-stage oligomerization catalyst produces a third oligomerized effluent stream in a third oligomerized effluent line 324c at an elevated outlet temperature. In an embodiment, the third oligomerized effluent stream is a penultimate oligomerized effluent stream and the third oligomerized effluent line 324c is a penultimate oligomerized effluent line 324c. The elevated outlet temperature is limited to between 30°C (54°F) and 50°C (90°F) above the inlet temperature to the catalyst bed 322c.

[0100] The third oligomerized effluent stream in line 324c removed from the second, first-stage oligomerization reactor vessel 321b of the first-stage oligomerization reactor 322

may be mixed with the fourth recycle olefin stream in line 326d to provide a second recycle olefin charge stream in line 316d. The third oligomerized effluent stream in line 324c includes the diluent stream from diluent line 314 added to the first olefin stream in line 312a. None of the charge olefin stream in line 312 is directly added to the second recycle olefin charge stream in line 316d. In an embodiment, the third oligomerized effluent stream in line 324c may also be mixed with an olefin charge stream from the olefin charge line 322 and be oligomerized therewith. The second recycle olefin charge stream may comprise no more than 35 wt% C2 to C8 olefins, suitably no more than 30 wt% C2 to C8 olefins and preferably no more than 25 wt% C2 to C8 olefins. The second recycle olefin charge stream may comprise no more than 30 wt% ethylene, suitably no more than 25 wt% ethylene and preferably no more than 20 wt% ethylene. The second recycle olefin charge stream may comprise no more than 30 wt% propylene, suitably no more than 25 wt% propylene and preferably no more than 20 wt% propylene. The second recycle olefin charge stream in line 316d may be cooled in a fourth charge cooler 318d which may be located externally to the second vessel 321b of the first-stage oligomerization reactor 322 to provide a cooled second recycle olefin charge stream in line 320d and charged to a fourth bed 322d of first-stage oligomerization catalyst in the second vessel of the first-stage oligomerization reactor 322. The charge cooler 318d may comprise a steam generator.

[0101] The cooled second recycle olefin charge stream in line 320d may be charged at a temperature of 180°C (356°F) to 230°C (446°F) and a pressure of 3.5 MPa (g) (500 psig) to 8.4 MPa (g) (1200 psig). The cooled second recycle olefin charge stream in line 320d will include diluent and olefins from the third or penultimate oligomerized effluent stream and C4-C8 olefins from the fourth recycle olefin stream. The olefins will oligomerize over the fourth catalyst bed 322d. Oligomerization of ethylene and propylene in the second recycle olefin charge stream in the fourth bed 322d of first-stage oligomerization catalyst produces a fourth oligomerized stream in a fourth oligomerized effluent line 324d at an elevated outlet temperature. The elevated outlet temperature is limited to between 30°C (54°F) and 50°C (90°F) above the inlet temperature to the catalyst bed 322d.

[0102] The fourth oligomerized effluent stream in line 324d exits the second reactor vessel 321b of the first-stage oligomerization reactor 322. In an embodiment, the fourth oligomerized effluent stream in line 324d is a last oligomerized effluent stream, and the fourth oligomerized effluent line 324d is a last oligomerized effluent line 324d.

[0103] The first-stage oligomerization reaction takes place predominantly in the liquid phase or in a mixed liquid and gas phase at a LHSV 0.5 to 10 hr⁻¹ on an olefin basis. We have found that across the first-stage oligomerization catalyst beds, typically 30-50 wt% ethylene in the olefin stream converts to higher olefins. The ethylene will initially dimerize over the catalyst to butenes. A predominance of the propylene and butenes in the olefins stream charged to a first-stage oligomerization catalyst bed is oligomerized. In an embodiment, at least 99 mol% of propylene and butenes in the olefins stream are oligomerized.

[0104] The first-stage oligomerization catalyst may include a zeolitic catalyst. The first-stage oligomerization catalyst may be considered a solid acid catalyst. The zeolite may comprise between 5 and 95 wt% of the catalyst, for example between 5 and 85 wt%. Suitable zeolites include zeolites having a structure from one of the following classes: MFI, MEL, ITH, IMF, TUN, FER, BEA, FAU, BPH, MEL, MSE, MWW, UZM-8, MOR, OFF, MTW, TON, MTT, AFO, ATO, and AEL. Three-letter codes indicating a zeotype are as defined by the Structure Commission of the International Zeolite Association and are maintained at <http://www.iza-structure.org/databases>. UZM-8 is as described in U.S. Pat. No. 6,756,030. In a preferred aspect, the first-stage oligomerization catalyst may comprise a zeolite with a framework having a ten-ring pore structure. Examples of suitable zeolites having a ten-ring pore structure include TON, MTT, MFI, MEL, AFO, AEL, EUO and FER. In a further preferred aspect, the first-stage oligomerization catalyst comprising a zeolite having a ten-ring pore structure may comprise a uni-dimensional pore structure. A uni-dimensional pore structure indicates zeolites containing non-intersecting pores that are substantially parallel to one of the axes of the crystal. The pores preferably extend through the zeolite crystal. Suitable examples of zeolites having a ten-ring uni-dimensional pore structure may include MTT. In a further aspect, the first-stage oligomerization catalyst comprises an MTT zeolite.

[0105] The first-stage oligomerization catalyst may be formed by combining the zeolite with a binder, and then forming the catalyst into pellets. The pellets may optionally be treated with a phosphorus reagent to create a zeolite having a phosphorous component between 0.5 and 15 wt % of the treated catalyst. The binder is used to confer hardness and strength on the catalyst. Binders include alumina, aluminum phosphate, silica, silica-alumina, zirconia, titania and combinations of these metal oxides, and other refractory oxides, and clays such as

montmorillonite, kaolin, palygorskite, smectite and attapulgite. A preferred binder is an aluminum-based binder, such as alumina, aluminum phosphate, silica-alumina and clays.

5 [0106] One of the components of the catalyst binder utilized in the present disclosure is alumina. The alumina source may be any of the various hydrous aluminum oxides or alumina gels such as alpha-alumina monohydrate of the boehmite or pseudo-boehmite structure, alpha-alumina trihydrate of the gibbsite structure, beta-alumina trihydrate of the bayerite structure, and the like. A suitable alumina is available from UOP LLC under the trademark VERSAL. A preferred alumina is available from Sasol North America Alumina Product Group under the trademark CATAPAL. This material is an extremely high purity alpha-
10 alumina monohydrate (pseudo-boehmite) which after calcination at a high temperature has been shown to yield a high purity gamma-alumina.

[0107] A suitable first-stage oligomerization catalyst is prepared by mixing proportionate volumes of zeolite and alumina to achieve the desired zeolite-to-alumina ratio. In an embodiment, the MTT content may 5 to 85, for example 20 to 82 wt% MTT zeolite, and the
15 balance alumina powder will provide a suitably supported catalyst. A silica support is also contemplated.

[0108] Monoprotic acid such as nitric acid or formic acid may be added to the mixture in aqueous solution to peptize the alumina in the binder. Additional water may be added to the mixture to provide sufficient wetness to constitute a dough with sufficient consistency to be
20 extruded or spray dried. Extrusion aids such as cellulose ether powders can also be added. A preferred extrusion aid is available from The Dow Chemical Company under the trademark Methocel.

[0109] The paste or dough may be prepared in the form of shaped particulates, with the preferred method being to extrude the dough through a die having openings therein of desired
25 size and shape, after which the extruded matter is broken into extrudates of desired length and dried. A further step of calcination may be employed to give added strength to the extrudate. Generally, calcination is conducted in a stream of air at a temperature from 260°C (500°F) to 815°C (1500°F). The MTT catalyst is not selectivated to neutralize acid sites such as with an amine.

30 [0110] The extruded particles may have any suitable cross-sectional shape, i.e., symmetrical or asymmetrical, but most often have a symmetrical cross-sectional shape, preferably a spherical, cylindrical or polylobal shape. The cross-sectional diameter of the

particles may be as small as 40 μm ; however, it is usually 0.635 mm (0.25 inch) to 12.7 mm (0.5 inch), preferably 0.79 mm (1/32 inch) to 6.35 mm (0.25 inch), and most preferably 0.06 mm (1/24 inch) to 4.23 mm (1/6 inch).

5 [0111] In one exemplary embodiment, an MTT-type zeolite catalyst disposed on a high purity pseudo boehmite alumina substrate in a ratio of 90/10 to 20/80 and preferably between 20/80 and 50/50 is provided in a catalyst bed or more in the first-stage oligomerization reactor 322.

[0112] The first-stage oligomerization catalyst can be regenerated upon deactivation. Suitable regeneration conditions include subjecting the first-stage oligomerization catalyst, 10 for example, in situ, to hot air at 400 to 500°C for 3 hours. To facilitate regeneration without downtime, a swing bed arrangement may be employed with an alternative first-stage oligomerization reactor. A regeneration gas stream may be admitted to the first-stage oligomerization reactor 322 requiring regeneration. The regeneration gas may comprise air with an increased or decreased concentration of oxygen. Activity and selectivity of the 15 regenerated catalyst is comparable to fresh catalyst.

[0113] The zeolite catalyst is advantageous as a first-stage oligomerization catalyst. The zeolitic catalyst has relatively low sensitivity towards oxygenates contamination. Consequently, a smaller degree of removal of oxygenates is required of olefinic feed in line 312 if produced from an ethanol dehydration process.

20 [0114] The last first-stage oligomerized stream in the last first-stage oligomerized effluent line 324d has an increased concentration of ethylene and propylene oligomers compared to the charge olefin stream in line 312. The last first-stage oligomerized stream in the last first-stage oligomerized effluent line 324d is cooled by steam generation in a steam generator 318e or by other heat exchange and further cooled by heat exchange against a 25 second stage oligomerized stream in line 334 and perhaps further cooled such as by an air cooler to provide a charge first-stage oligomerized stream and charged to a second-stage oligomerization reactor 332 in a second-stage oligomerization charge line 328. To achieve the most desirable olefin product, the second-stage oligomerization reactor 332 is operated at a temperature from 80°C (176°F) to 180°C (356°F). The second-stage oligomerization 30 reactor 332 is run at a pressure from 2.1 MPa (300 psig) to 7.6 MPa (1100 psig), and more preferably from 3.5 MPa (500 psig) to 6.9 MPa (1000 psig).

[0115] The second-stage oligomerization reactor 332 may be in downstream communication with the first-stage oligomerization reactor 322. The second-stage oligomerization reactor 332 preferably operates in a down flow operation. However, upflow operation may be suitable. The second-stage oligomerization charge stream is contacted with the second-stage oligomerization catalyst causing the unconverted ethylene from the first-stage oligomerization reactor 322 to dimerize and trimerize while higher olefins also dimerize, trimerize and tetramerize to provide distillate range olefins. With regard to the second-stage oligomerization reactor 332, process conditions are selected to produce a higher percentage of jet range olefins which, when hydrogenated in a subsequent step, result in a desirable jet-range hydrocarbon product. A predominance of the unconverted ethylene from the first-stage oligomerization reactor 322 is dimerized, trimerized and tetramerized. In an embodiment, at least 99 wt% of ethylene in the second-stage oligomerization charge stream is converted to mostly butenes.

[0116] The second-stage oligomerization reactor 332 may comprise a first reactor vessel 331a comprising a first bed 332a of second-stage oligomerization catalyst and a second reactor vessel 331b comprising a second bed 332b of second-stage oligomerization catalyst. A first, second-stage oligomerized stream is discharged from the first, second-stage reactor vessel 331a, cooled and charged to the second, second-stage reactor vessel 331b. A second-stage oligomerized stream with an increased average carbon number greater than the charge first-stage oligomerized stream in line 328 exits the second-stage oligomerization reactor 332 in line 334.

[0117] The second-stage oligomerization catalyst is preferably an amorphous silica-alumina base with a metal from either Group VIII and/or Group VIB in the periodic table using Chemical Abstracts Service notations. In an aspect, the catalyst has a Group VIII metal promoted with a Group VIB metal. Typically, the silica and alumina will only be in the base, so the silica-to-alumina ratio will be the same for the catalyst as for the base. The metals can either be impregnated onto or ion exchanged with the silica-alumina base. Co-mulling is also contemplated. Catalysts for the present disclosure may have a Low Temperature Acidity Ratio of at least 0.15, suitably of 0.2, and preferably greater than 0.25, as determined by Ammonia Temperature Programmed Desorption (Ammonia TPD) as described hereinafter. Additionally, a suitable catalyst will have a surface area of between 50 and 400 m²/g as determined by nitrogen BET.

[0118] The preferred second-stage oligomerization catalyst comprises an amorphous silica-alumina support. One of the components of the catalyst support utilized in the present disclosure is alumina. The alumina may be any of the various hydrous aluminum oxides or alumina gels such as alpha-alumina monohydrate of the boehmite or pseudo-boehmite structure, alpha-alumina trihydrate of the gibbsite structure, beta-alumina trihydrate of the bayerite structure, and the like. A particularly preferred alumina is available from Sasol North America Alumina Product Group under the trademark CATAPAL. This material is an extremely high purity alpha-alumina monohydrate (pseudo-boehmite) which after calcination at a high temperature has been shown to yield a high purity gamma-alumina. Another component of the catalyst support is an amorphous silica-alumina. A suitable silica-alumina with a silica-to-alumina ratio of 2.6 is available from CCIC, a subsidiary of JGC, Japan.

[0119] Another component utilized in the preparation of the second-stage oligomerization catalyst utilized in the present disclosure is a surfactant. The surfactant is preferably admixed with the hereinabove described alumina and the silica-alumina powders. The resulting admixture of surfactant, alumina and silica-alumina is then formed, dried and calcined as hereinafter described. The calcination effectively removes by combustion the organic components of the surfactant but only after the surfactant has dutifully performed its function in accordance with the present disclosure. Any suitable surfactant may be utilized in accordance with the present disclosure. A preferred surfactant is a surfactant selected from a series of commercial surfactants sold under the trademark "Antarox" by Solvay S.A. The "Antarox" surfactants are generally characterized as modified linear aliphatic polyethers and are low-foaming biodegradable detergents and wetting agents.

[0120] A suitable silica-alumina mixture is prepared by mixing proportionate volumes silica-alumina and alumina to achieve the desired silica-to-alumina ratio. In an embodiment, 75 to 99 wt-% amorphous silica-alumina with a silica-to-alumina ratio of 2.6 and 10 to 20 wt-% alumina powder will provide a suitable support. In an embodiment, other ratios of amorphous silica-alumina to alumina may be suitable.

[0121] Any convenient method may be used to incorporate a surfactant with the silica-alumina and alumina mixture. The surfactant is preferably admixed during the admixture and formation of the alumina and silica-alumina. A preferred method is to admix an aqueous solution of the surfactant with the blend of alumina and silica-alumina before the final

formation of the support. It is preferred that the surfactant be present in the paste or dough in an amount from 0.01 to 10 wt-% based on the weight of the alumina and silica-alumina.

[0122] Monoprotic acid such as nitric acid or formic acid may be added to the mixture in aqueous solution to peptize the alumina in the binder. Additional water may be added to the mixture to provide sufficient wetness to constitute a dough with sufficient consistency to be extruded or spray dried.

[0123] The paste or dough may be prepared in the form of shaped particulates, with the preferred method being to extrude the dough mixture of alumina, silica-alumina, surfactant and water through a die having openings therein of desired size and shape, after which the extruded matter is broken into extrudates of desired length and dried. A further step of calcination may be employed to give added strength to the extrudate. Generally, calcination is conducted in a stream of dry air at a temperature from 260°C (500°F) to 815°C (1500°F).

[0124] The extruded particles may have any suitable cross-sectional shape, i.e., symmetrical or asymmetrical, but most often have a symmetrical cross-sectional shape, preferably a spherical, cylindrical or polylobal shape. The cross-sectional diameter of the particles may be as small as 40 µm; however, it is usually 0.635 mm (0.25 inch) to 12.7 mm (0.5 inch), preferably 0.79 mm (1/32 inch) to 6.35 mm (0.25 inch), and most preferably 0.06 mm (1/24 inch) to 4.23 mm (1/6 inch).

[0125] Typical characteristics of the amorphous silica-alumina supports utilized herein are a total pore volume, average pore diameter and surface area large enough to provide substantial space and area to deposit the active metal components. The total pore volume of the support, as measured by conventional mercury porosimeter methods, is usually 0.2 to 2.0 cc/gram, preferably 0.25 to 1.0 cc/gram and most preferably 0.3 to 0.9 cc/gram. Ordinarily, the amount of pore volume of the support in pores of diameter greater than 100 angstroms is less than 0.1 cc/gram, preferably less than 0.08 cc/gram, and most preferably less than 0.05 cc/gram. Surface area, as measured by the B.E.T. method, is typically above 50 m²/gram, e.g., above 200 m²/gram, preferably at least 250 m²/gram., and most preferably 300 m²/gram to 400 m²/gram.

[0126] To prepare the second-stage oligomerization catalyst, the support material is compounded, as by a single impregnation or multiple impregnations of a calcined amorphous refractory oxide support particles, with one or more precursors of at least one metal component from Group VIII or VIB of the periodic table. The Group VIII metal, preferably

nickel, should be present in a concentration of 0.5 to 15 wt-% and the Group VIB metal, preferably tungsten, should be present in a concentration of 0 to 12 wt-%. The impregnation may be accomplished by any method known in the art, as for example, by spray impregnation wherein a solution containing the metal precursors in dissolved form is sprayed onto the

5 support particles. Another method is the multi-dip procedure wherein the support material is repeatedly contacted with the impregnating solution with or without intermittent drying. Yet other methods involve soaking the support in a large volume of the impregnation solution or circulating the support therein, and yet one more method is the pore volume or pore

10 saturation technique wherein support particles are introduced into an impregnation solution of volume just sufficient to fill the pores of the support. On occasion, the pore saturation technique may be modified, so as to utilize an impregnation solution having a volume between 10 percent less and 10 percent more than that which will just fill the pores.

[0127] If the active metal precursors are incorporated by impregnation, a subsequent or second calcination at elevated temperatures, as for example, between 399°C (750°F) and

15 760°C (1400°F), converts the metals to their respective oxide forms. In some cases, calcinations may follow each impregnation of individual active metals. A subsequent calcination yields a catalyst containing the active metals in their respective oxide forms.

[0128] A preferred second-stage oligomerization catalyst of the present disclosure has an amorphous silica-alumina base impregnated with 0.5 to 15 wt-% nickel in the form of 3.175

20 mm (0.125 inch) extrudates and a density of 0.45 to 0.65 g/ml. It is also contemplated that metals can be incorporated onto the support by other methods such as ion-exchange and co-mulling.

[0129] The second-stage oligomerization catalyst can be regenerated upon deactivation. Suitable regeneration conditions include subjecting the catalyst, for example, in situ, to hot

25 air at 400 to 500°C for 3 hours. To facilitate regeneration without downtime, a swing bed arrangement may be employed with an alternative second-stage oligomerization reactor. The regeneration gas may comprise air with an increased or decreased concentration of oxygen. Activity and selectivity of the regenerated catalyst is comparable to fresh catalyst.

[0130] Second-stage oligomerization reactions are also exothermic in nature. The last

30 oligomerized olefin stream in line 324d includes the diluent stream from diluent line 314 added to the first olefin stream in line 312a and carried through the first-stage oligomerization catalyst beds 322a-322d. The diluent stream is then transported into the second-stage

oligomerization reactor 332 in line 328 to absorb the exotherm in the second-stage oligomerization reactor. A dedicated diluent line to second-stage oligomerization reactor 332 is also contemplated for prompt control of exotherm rise or to cool down the second-stage oligomerization reactor 332 and want to cool down only second stage.

5 **[0131]** When the oligomerization reaction is performed according to the above-noted process conditions, a C4 olefin conversion of greater than or equal to 95% is achieved, or greater than or equal to 97%. The resulting second-stage oligomerized stream in line 334 includes a plurality of olefin products that are distillate range hydrocarbons.

10 **[0132]** An oligomerized olefin stream in line 334 with an increased C8+ olefin concentration compared to the charge first-stage oligomerization stream in line 328 is heat exchanged with the first-stage oligomerized stream in line 324d, let down in pressure, subsequently heat exchanged with an olefin splitter bottoms stream in line 30 and fed to a dealkanizer column 340. The oligomerized olefin stream in line 334 is at a temperature from 160°C (320°F) to 190°C (374°F) and a pressure of 3.9 MPa (gauge) (550 psig) to 7 MPa
15 (gauge) (1000 psig). The olefin splitter bottoms stream in line 330 may be transported to a hydrogenation section.

20 **[0133]** We have found that light alkanes such as ethane and/or propane are generated in the first-stage oligomerization reactor 322 and/or the second-stage oligomerization reactor 332 which must be removed from the second-stage oligomerized stream for fuels production particularly to facilitate light olefin recycle to the first-stage oligomerization reactor 322. Light alkanes are inert and would accumulate in the recycle loop. Hence, the second-stage oligomerized stream in line 334 is dealkanized by fractionation in a dealkanizer column 340 to provide a light alkane stream and a dealkanized stream. In an embodiment, the light
25 alkane stream is an ethane stream in which case the dealkanizer column 340 is a deethanizer column. In another embodiment, the light alkane stream is a propane stream in which case the dealkanizer column 340 is a depropanizer column. The alkane stream may also be a mixture of ethane and propane. The alkane stream may be used as fuel for providing heating duty in the process 310.

30 **[0134]** In the dealkanizer column 340, light alkanes such as C3- and suitably C2- hydrocarbons, are separated perhaps in an alkane overhead stream in an overhead line 342 of FIG. 3 from perhaps a dealkanized bottoms stream in a bottoms line 344 comprising C4+ and suitably C3+ hydrocarbons. The dealkanizer column 340 may be operated at a bottoms

temperature of 177°C (350°F) to 302°C (575°F) and an overhead pressure of 207 kPa (gauge) (30 psig) to 690 kPa (gauge) (100 psig) if operated as a deethanizer column. The dealkanizer column 340 may be operated at a bottoms temperature of 194°C (381°F) to 333°C (630°F) and an overhead pressure of 207 kPa (gauge) (30 psig) to 1.14 MPa (gauge) (165 psig) if operated as a depropanizer column.

5 [0135] The alkane overhead stream in the overhead line 342 may be cooled and separated in a dealkanizer receiver 346 to provide a dealkanized off-gas in an off-gas line 347 in which it may be chilled and fed to further processing such as to be taken as fuel gas in line 348 along with a net vapor stream in a receiver overhead line 368. Condensate from the
10 dealkanizer receiver 344 may be refluxed back to the dealkanizer column 340 in a dealkanizer overhead liquid line 349. In an embodiment, some of the condensate from the dealkanizer receiver 344 in line 349 may be taken as recycle in line 351 to the first stage oligomerization reactor in lines 372 and 326. The dealkanized stream perhaps in the bottoms line 344 may be split between a reboil stream in line 350 which is reboiled by heat exchange
15 with a first hot diesel stream in line 352 perhaps taken from a jet fractionator bottom heat exchange stream in the jet bottoms heat exchange line 374 and a net bottoms stream in line 354 which is fed directly to an olefin splitter column 360 perhaps without heating. The reboiled bottom stream in line 350 may be returned boiling to the dealkanizer column 340 to provide heating requirements. In another embodiment, feed to dealkanizer column 340 is not
20 preheated by olefin splitter bottoms stream in line 330, but the feed to the olefins splitter column 360 in the net bottoms line 354 would be preheated by olefin splitter bottoms stream.

[0136] The dealkanized stream in the dealkanizer net bottoms line 354 is split by fractionation in an olefin splitter column 360 into a light olefin stream perhaps in an olefin splitter overhead line 362 and a heavy olefin stream perhaps in an olefin splitter bottoms line
25 364. The olefin splitter overhead stream may be cooled to 66°C (150°F) to 93°C (200°F) and a resulting condensate portion refluxed from an olefin splitter receiver 366 back to the olefin splitter column 360. The net vapor stream in the receiver overhead line 368 from the olefin splitter receiver 366 may be chilled and further processed such as fuel gas in line 348 along with the off-gas stream in the off-gas line 347. The light olefin condensate from a bottom of
30 the olefin splitter receiver in line 370 may be split between a reflux stream that is refluxed back to the column in line 371 and a light olefin recycle stream in a recycle line 372 that may be recycled to the first-stage oligomerization reactor 322 or alternatively to the second-stage

oligomerization reactor 332. The light olefin stream in line 372 may comprise 1 to 15 wt% of the light olefin stream in line 370. The light olefin stream in line 372 may comprise 40 to 80 wt% C4-C8 olefins. In an embodiment, the light olefin stream in line 372 may be flashed in a knock-out drum 375 to remove vapors in a light olefin vapor stream which may be

5 transported to a hydrogenation section in an overhead line 377 and the liquid recycle olefin oligomer stream in line 326 may be recycled to the first-stage oligomerization reactor 322 to oligomerize the C4-C8 olefins.

[0137] The stream exiting the depropanizer in the oligomerization process will be sent to a reactor where it will be converted to syngas via steam reforming, partial oxidation,
10 autothermal reforming, or dry reforming. Syngas will then be sent to the methanol synthesis unit. If partial oxidation or autothermal reforming is selected to produce the syngas, air or oxygen must also be provided, and additional steam could be extracted from the reactor for use elsewhere in the facility. If steam reforming is selected to produce the syngas from ethane/propane, it will also need steam feeds (which could be fully supplied by the Methanol
15 to Jet process) and energy input (which could be partially supplied by steam from Methanol To Jet process).

Reforming

[0138] A syngas stream comprising carbon oxides and hydrogen may be produced by reforming the alkane overhead stream in the overhead line 342 of FIG. 3 with steam in a
20 steam reforming reactor, an autothermal reforming reactor, or a dry reforming reactor.

Steam Reforming

[0139] Steam reforming the alkane overhead stream from overhead line 342 of FIG. 3 at high temperatures with CO₂ and steam will create a syngas mixture that can be fed directly to methanol synthesis. This is an endothermic process so requires a substantial amount of
25 external heat.

[0140] The alkane overhead stream 342 is mixed with one to two carbon equivalent of carbon dioxide to prevent elemental carbon production. The alkane stream and carbon dioxide mixture is then mixed with steam to produce a mixture containing 1 mol carbon from hydrocarbons to 1-2 mole water. The gas/steam mixture enters a steam reforming process unit
30 charged with commercially available Nicel catalyst. The conversion of the hydrocarbons to carbon monoxide and hydrogen takes place at 700° C-900° C at a system pressure that may be between 12 and 500 psia. A typical flow rate for such reactor would be 300 lbs/hr/cubic

feet of catalyst. After condensation of the water the product gas from the steam reforming may be fed directly to the syngas mixer or may be freed from carbon dioxide and other minor components first, depending on the intended application of the syngas.

Autothermal Reforming

- 5 [0141] Autothermal reforming combines both partial oxidation and steam reforming. Oxygen from the hydrolysis unit, steam, and CO₂ are reacted over a catalyst to produce an appropriate syngas mixture for conversion to methanol.
- [0142] The alkane overhead stream from overhead line 342 of FIG. 3 is reacted in an autothermal reactor to produce a recycle syngas stream comprising largely CO and hydrogen.
- 10 Heat from the exothermic partial oxidation helps driving the endothermic steam reforming process. The resultant syngas can be recycled into the methanol synthesis unit.

Dry Reforming

- [0143] Dry reforming is an endothermic reaction between methane and carbon dioxide to produce carbon monoxide and hydrogen. The alkane overhead stream from overhead line
- 15 342 of FIG. 3 is reacted in a dry reformer to produce the syngas. The resultant syngas can be recycled into the methanol synthesis unit.

Partial Oxidation

- [0144] Alternatively, a syngas stream comprising carbon oxides and hydrogen may be produced by partially oxidizing the alkane overhead stream from overhead line 342 of FIG. 3
- 20 in a partial oxidation reactor with oxygen.

Hydrogen Recycling

- [0145] It has been found that hydrogen from the hydrogen generator such as a reformer or electrolyzer can first be sent to the hydrocarbon hydrogenation reactor to produce renewable fuels. Excess hydrogen and any other off-gases flashed off in a separation drum would then
- 25 be sent to the CO₂ hydrogenation reactor to make methanol. Excess hydrogen from the CO₂ hydrogenation reactor would then be compressed, purified (if needed) and recycled to the hydrocarbon hydrogenation reactor, where it would be mixed with the fresh hydrogen from the hydrogen generator. A purge of hydrogen in the recycle may be necessary. Hydrogen from the hydrogen generator can first be sent to the CO₂ hydrogenation reactor to produce
- 30 methanol. Excess hydrogen and any other offgases flashed off in a separation drum would then be send to the hydrocarbon hydrogenation reactor to make renewable fuels. Excess hydrogen from the hydrocarbon hydrogenation reactor would then be compressed, purified (if

needed) and recycled to the CO₂ hydrogenation reactor, where it would be mixed with the fresh H₂ from the H₂ generator. A purge of H₂ in the recycle may be necessary.

[0146] FIG. 4 shows a general flow scheme with the hydrogen recycle. A carbon dioxide stream 500 is sent to a methanol synthesis unit 502. Crude methanol stream 503 is then sent to a methanol purification unit 504 with a green feed methanol 530 then being sent to methanol to olefins vaporization section 528. A dry methanol and recovered dimethyl ether stream 529 is then sent to a methanol to olefins reactor and regeneration unit 525 with a product stream 524 sent to a light olefins recovery process 522. An offgas stream 523 is removed, a dried liquid and vapor olefin product stream 540 and a water recycle or water removal stream 526 is shown. The stream 540 is then sent to a light olefins recovery process section 521 to produce a purified liquid and vapor olefins stream 520 which is sent to oligomerization section 516, with offgas 517, recycle oil 513 and a C₉+ olefins stream 515. C₉+ olefins stream 515 is sent to a hydrogenation section 512 from which offgas stream 511, sustainable aircraft fuel 510, recoverable diesel and naphtha stream 509 exit. Also shown is a recycle hydrogen stream 514 from the hydrogenation section 512 that is sent to the light olefins recovery process to be used in selective hydrogenation or other processes requiring hydrogen. In the lower left is shown a hydrogen production unit 508 which may be an electrolyzer or reformer such as those described above. Hydrogen 507 from methanol synthesis unit 502 may be recycled and used in the hydrogenation unit 512.

[0147] FIG. 5 shows the light olefins recovery part of the process after fractionation and concentration. A dried olefin liquid 602 is pumped to be combined with dried olefin vapor stream 604 and enter a demethanizer feed chiller 606 cooled by refrigeration equipment 608. The chilled olefins are sent to a demethanizer column 610 with offgas 612 exiting and the olefins then going to a deethanizer column 614. Part of the recycled hydrogen stream 616 is added after being separated from the hydrogenation unit and then going to acetylene converter 618. The olefins then pass through water and carbon dioxide guard beds 620 with a purified olefin stream 622 sent to the oligomerization section. The bottom stream from the deethanizer column 614 is sent to a DME wash column 624 and a DME wash water stripper column 626 so that recovered DME can be sent to the methanol to olefin reactor through line 628. An overhead stream from the DME wash column is sent to a selective hydrogenation unit 634 together with some C₄+ olefins from the DME stripper. The selective hydrogenation unit 634 is in fluid downstream communication with the DME wash column 624. A portion

of the hydrogen 636 that is recycled from the hydrogenation unit is shown added and then the hydrogenated product is sent to an oxygenates removal unit 642 with oxygenates 644 removed and a purified olefin stream 640 sent to oligomerization.

[0148] Fig. 6 shows the hydrogenation section of the process including the places that
5 hydrogen may be recycled to and from the process. C9+ olefin stream 700 is sent to a hydrogenation reactor 704 together with drag stream 702 from olefin splitter. The bottoms stream from the hydrogenation reactor is sent to a hot separator 706 followed by cold separator 710 with a hydrogen stream 708 produced that can be sent as needed in the process shown in Fig. 5 or to the methanol synthesis process. The remainder of the separated stream
10 is sent to flash stripper 712 and jet fuel fractionation column 732 to produce a renewable naphtha stream 736, jet fuel stream 734 that is a sustainable aviation fuel, and a renewable diesel stream 724. Also shown are a reboiler section 730 and 728. Recycled oil is sent in line 722 to the oligomerization section.

EXAMPLES

[0149] The examples below cascade hydrogen from a recycle stream in a dimerization and/or an oligomerization unit to two different units within the light olefin recovery process (LORP) section of the plant, referenced as LORP Unit 1 and LORP Unit 2 in the example. Base case simulations were developed utilizing appropriate components and fluid packages to address the requirements of the units being simulated.

EXAMPLE 1

- [0150] The cascaded hydrogen from a recycle stream was compared with a base case which utilizes fresh pure hydrogen. The base case passed fresh, pure hydrogen to the dimerization and/or oligomerization unit and to the two separate units LORP Unit 1 and LORP Unit 2 in the light olefin recovery process (LORP). The fresh, pure hydrogen is typically 99.9+ mol % hydrogen.
- [0151] The dimerization and/or oligomerization unit also has a hydrogen recycle stream, which recycles slightly impure hydrogen (~97% hydrogen) to the unit and also has a purge associated with it at the same composition, to prevent buildup of impurities in the oligomerization/dimerization hydrogen loop. One possible location for this purge stream was a fuel gas header in the plant. The cascaded hydrogen network passed fresh, pure hydrogen to the dimerization and/or oligomerization unit. However, it replaced fresh, pure hydrogen to LORP Unit 1 and LORP Unit 2 with the recycle hydrogen (~97% H₂) from the dimerization and/or oligomerization unit. The recycle hydrogen purge rate was left constant in this example. Table 1 below shows the material balances for both base and hydrogen cascaded cases for this example.

Table 1: Hydrogen Flow rates

	Units	Base Case	Cascaded Hydrogen Case
Fresh, Pure H ₂ to Oligomer/Dimer Unit	lbmol/hr	587.4	597.8
Fresh, Pure H ₂ to LORP Unit #1	lbmol/hr	1.5	0
Fresh, Pure H ₂ to LORP Unit #2	lbmol/hr	8.9	0
Total Fresh H ₂ Req.	lbmol/hr	597.8	597.8
Recycle H ₂ to Oligomer/Dimer Unit	lbmol/hr	378.0	367.3
Recycle H ₂ Purge	lbmol/hr	57.8	57.8
Cascaded Recycle H ₂ to LORP Unit #1	lbmol/hr	0	1.6
Cascaded Recycle H ₂ to LORP Unit #2	lbmol/hr	0	9.1
Total Recycle H ₂	lbmol/hr	435.8	435.8

[0152] The required hydrogen pressure for LORP Unit 1 and LORP Unit 2 were lower than the hydrogen pressure requirement for the oligomerization/dimerization unit. Table 2 below shows required pressure of hydrogen for the units.

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Table 2: Required Hydrogen Pressures

	Units	Hydrogen Required Pressure
Fresh H ₂ to Olig/Dimer Unit	psig	630
Fresh H ₂ to LORP Unit #1	psig	419
Fresh H ₂ to LORP Unit #2	psig	365

[0153] In the base case, hydrogen is compressed to 630 psig for all units and let down to the required pressure for the LORP Unit 1 and LORP Unit 2. In the cascaded case, all of the hydrogen was pressurized to 630 psig and utilized at 630 psig, because it is sent to the Oligomerization/Dimerization Unit. This minimizes wasted losses from compression by reducing the duty on the recycle hydrogen compressor by 3% while maintaining the same duty on the fresh, pure hydrogen compressor.

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EXAMPLE 2

[0154] Example 2 has the exact same basis as Example 1, but instead of holding the purge gas rate constant from the oligomerization/dimerization recycle loop, some of the purge gas from the recycle loop is used to supply the LORP Unit 1 and LORP Unit 2 with

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hydrogen. Similar to Example 1, the fresh, pure hydrogen was typically 99.9+ mol % hydrogen and the recycle hydrogen purity was 97 mol % hydrogen in this example.

- [0155] The purge gas pressure was 598 psig at the take-off, meaning no additional compression was needed to cascade the purge gas. Making this change reduced the amount of fresh, pure hydrogen needed to the overall system – helping to reduce costs of generating and compressing the fresh, pure H₂ by 2%. This also has the added benefit of reduced compression costs cited in Example 1. Table 3 shows the material balances for both base and hydrogen cascaded cases for this example.

Table 3: Hydrogen Flow rates

	Units	Base Case	Cascaded H2 Case
Fresh, Pure H ₂ to Olig/Dimer Unit	lbmol/hr	587.4	587.4
Fresh, Pure H ₂ to LORP Unit #1	lbmol/hr	1.5	0
Fresh, Pure H ₂ to LORP Unit #2	lbmol/hr	8.9	0
Total Fresh H ₂ Req.	lbmol/hr	597.8	587.4
Recycle H ₂ to Olig/Dimer Unit	lbmol/hr	378.0	378.0
Recycle H ₂ Purge	lbmol/hr	57.8	48.0
Cascaded Recycle H ₂ to LORP Unit #1	lbmol/hr	0	1.6
Cascaded Recycle H ₂ to LORP Unit #2	lbmol/hr	0	9.1
Total Recycle H ₂	lbmol/hr	436.7	436.7

SPECIFIC EMBODIMENTS

[0156] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

- 5 [0157] A first embodiment of the present disclosure is a process for providing hydrogen in a process to produce jet fuel from methanol comprising producing a supply of hydrogen from a hydrogen production unit to be sent to one or more vessels within said process and wherein additional supplies of hydrogen are recovered from reaction in which hydrogen is not fully consumed and taken in a recycle stream or recycle streams from one or more
- 10 reactors or vessels and sent to supplement said first supply of hydrogen. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said hydrogen production unit is an electrolyzer, steam reformer or autothermal reformer. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first
- 15 embodiment of this paragraph wherein said first supply of hydrogen is sent to a hydrogenation reactor and a methanol synthesis reactor. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said additional supply of hydrogen is a second supply of hydrogen that is recovered from a hydrogenation reactor downstream from an
- 20 oligomerization reactor. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said additional supply of hydrogen is a third supply of hydrogen that is recovered from a hydrogenation reactor downstream from a DME wash column in a light olefin recovery process section. An embodiment of the present disclosure is one, any or all of the
- 25 prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said additional supply of hydrogen is a fourth supply of hydrogen that is recovered from a methanol synthesis unit. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said second supply of hydrogen is sent from said hydrogenation reactor to a selective
- 30 hydrogenation reactor within a light olefin recovery process section of said process. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said second supply of

hydrogen is sent from said hydrogenation reactor to an acetylene conversion reactor within a light olefin recovery process section of said process. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein a portion of said second supply of hydrogen is sent to a methanol synthesis unit. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said third supply of hydrogen is sent from said hydrogenation reactor to an acetylene conversion reactor within a light olefin recovery process (LORP) section of said process. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein a portion of said third supply of hydrogen is sent to a methanol synthesis unit. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said fourth supply of hydrogen is sent to a hydrogenation reactor which is downstream of an oligomerization reactor. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said fourth supply of hydrogen is sent from said hydrogenation reactor to a selective hydrogenation reactor within a Light Olefin Recovery Process (LORP) section of said process. An embodiment of the present disclosure is one, any or all of the prior embodiments in this paragraph up through the first embodiment of this paragraph wherein said fourth supply of hydrogen is sent from said hydrogenation reactor to an acetylene conversion reactor within a light olefin recovery process (LORP) section of said process.

[0158] A second embodiment of the present disclosure is a process for providing hydrogen in a process to produce jet fuel from methanol comprising producing a supply of hydrogen from a hydrogen production unit to be sent to one or more vessels within the process and wherein additional supplies of hydrogen are recovered from reaction in which hydrogen is not fully consumed and recovered from a purification unit in a recycle stream or recycle streams from one or more reactors or vessels and sent to supplement the first supply of hydrogen. An embodiment of the present disclosure is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the hydrogen production unit is an electrolyzer, steam reformer or autothermal reformer. An embodiment of the present disclosure is one, any or all of prior embodiments in this

paragraph up through the second embodiment in this paragraph wherein the first supply of hydrogen is sent to a hydrogenation reactor and a methanol synthesis reactor. An embodiment of the present disclosure is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the additional supply of hydrogen is a
5 second supply of hydrogen that is recovered from a hydrogenation reactor downstream from an oligomerization reactor.

[0159] A third embodiment of the present disclosure is a process for providing hydrogen in a process to produce jet fuel from methanol comprising producing a supply of hydrogen from a hydrogen production unit to be sent to one or more vessels within the process, wherein
10 the hydrogen production unit is an electrolyzer, steam reformer or autothermal reformer, and wherein additional supplies of hydrogen are recovered from reaction in which hydrogen is not fully consumed and recovered from a purification unit in a recycle stream or recycle streams from one or more reactors or vessels and sent to supplement the first supply of hydrogen. An embodiment of the present disclosure is one, any or all of prior embodiments in
15 this paragraph up through the third embodiment in this paragraph wherein the first supply of hydrogen is sent to a hydrogenation reactor and a methanol synthesis reactor.

[0160] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present disclosure to its fullest extent and easily ascertain the essential characteristics of this disclosure, without departing from the spirit and scope
20 thereof, to make various changes and modifications of the present disclosure and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

25 **[0161]** In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS

1. A process for providing hydrogen in a process to produce jet fuel from methanol comprising producing a supply of hydrogen from a hydrogen production unit to be sent to one or more vessels within said process and wherein additional supplies of hydrogen are recovered from reaction in which hydrogen is not fully consumed and taken in a recycle stream or recycle streams from one or more reactors or vessels and sent to supplement said first supply of hydrogen.
2. The process of claim 1 wherein said hydrogen production unit is an electrolyzer, steam reformer or autothermal reformer.
3. The process of claim 2 wherein said first supply of hydrogen is sent to a hydrogenation reactor and a methanol synthesis reactor.
4. The process of claim 1 wherein said additional supply of hydrogen is a second supply of hydrogen that is recovered from a hydrogenation reactor downstream from an oligomerization reactor.
5. The process of claim 1 wherein said additional supply of hydrogen is a third supply of hydrogen that is recovered from a hydrogenation reactor downstream from a DME wash column in a light olefin recovery process section.
6. The process of claim 1 wherein said additional supply of hydrogen is a fourth supply of hydrogen that is recovered from a methanol synthesis unit.
7. The process of claim 4 wherein said second supply of hydrogen is sent from said hydrogenation reactor to a selective hydrogenation reactor within a light olefin recovery process section of said process; to an acetylene conversion reactor within a light olefin recovery process section of said process or to a methanol synthesis unit.
8. The process of claim 5 wherein said third supply of hydrogen is sent from said hydrogenation reactor to an acetylene conversion reactor within a light olefin recovery process (LORP) section of said process or to a methanol synthesis unit.
9. The process of claim 6 wherein said fourth supply of hydrogen is sent to a hydrogenation reactor which is downstream of an oligomerization reactor.
10. The process of claim 6 wherein said fourth supply of hydrogen is sent from said hydrogenation reactor to a selective hydrogenation reactor within a Light Olefin Recovery Process (LORP) section of said process.