

A RECYCLE OF BYPRODUCTS TO PROVIDE A GREEN HYDROGEN STREAM FOR A
METHANOL TO JET FUEL PROCESS

[0001] The field is the conversion of olefins to distillate. The field may particularly relate to the use of byproducts to produce hydrogen.

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BACKGROUND

[0002] 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 light olefins. The highly efficient Methanol to Olefin (MTO) process may convert oxygenates to light olefins which had been typically considered for plastics
10 production. Light olefins produced from the MTO process is highly concentrated in ethylene and propylene.

[0003] The ethanol dehydration process involves dehydration of ethanol molecules to generate ethylene and water. The process of converting ethanol to ethylene is endothermic in nature and the heat of endothermicity is typically provided by fired heaters to an adiabatic
15 reactor.

[0004] Ethylene can be oligomerized into olefins such as C₄, C₆ and C₈ olefins. Propylene can be oligomerized into olefins such as C₆, C₉ and C₁₂ olefins. Olefin oligomerization is a process that can oligomerize smaller olefins into larger olefins. More specifically, it can convert olefins including oligomerized olefins into distillates including jet fuel and diesel range products.
20 The oligomerized distillate can be saturated for use as transportation fuels.

[0005] 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.

25 [0006] The oligomerization unit requires hydrogen in order to meet the requirements for sustainable jet fuel. An improved process is provided to recycle hydrogen-rich off-gas streams to supplement the hydrogen produced by reforming.

DEFINITIONS

- [0007] The term “communication” means that fluid flow is operatively permitted between enumerated components, which may be characterized as “fluid communication”.
- 5 [0008] 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 with which it fluidly communicates.
- [0009] 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.
- 10 [0010] The term “direct communication” means that fluid flow from the upstream component enters the downstream component without passing through any other intervening vessel.
- [0011] The term “indirect communication” means that fluid flow from the upstream component enters the downstream component after passing through an intervening vessel.
- 15 [0012] The term “bypass” means that the object is out of downstream communication with a bypassing subject at least to the extent of bypassing.
- [0013] As used herein, the term “predominant” or “predominate” means greater than 50%, suitably greater than 75% and preferably greater than 90%.
- [0014] The term “column” means a distillation column or columns for separating one or
20 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 of the
25 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 bottom.
- 30 [0015] 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. As used herein, the term “boiling point temperature” means atmospheric equivalent boiling point (AEBP) as calculated from the observed boiling temperature and the distillation pressure, as calculated using the equations furnished in ASTM D1160 appendix A7 entitled “Practice for Converting Observed Vapor

Temperatures to Atmospheric Equivalent Temperatures”.
[0016] As used herein, the term “True Boiling Point” (TBP) means a test method for determining the boiling point of a material which corresponds to ASTM D-2892 for the production of a liquefied gas, distillate fractions, and residuum of standardized quality on which analytical data can be obtained, and the determination of yields of the above fractions by both mass and volume from which a graph of temperature versus mass % distilled is produced using fifteen theoretical plates in a column with a 5:1 reflux ratio.

[0017] 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.

[0018] As used herein, the term “initial boiling point” (IBP) means the temperature at which the sample begins to boil using ASTM D-7169, ASTM D-86 or TBP, as the case may be.

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

[0021] As used herein, the term “jet fuel” means hydrocarbons boiling in the range of a T10 between about 190°C (374°F) and about 215°C (419°F) and an end point of between about 290°C (554°F) and about 310°C (590°F). The term “green jet fuel” means jet fuel comprising hydrocarbons not sourced from fossil fuels.

[0022] As used herein, the term “predominant” or “predominate” means greater than 50%, suitably greater than 75% and preferably greater than 90%.

[0023] 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 feed to the vessel and preferably than all other streams withdrawn from the vessel.

[0024] 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.

[0025] As used herein, the term “rich” means greater than 50%, suitably greater than 75% and preferably greater than 90%.

[0026] 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.

15 DETAILED DESCRIPTION

[0027] A process is provided for converting methanol to jet fuel. This process may start with methanol derived from a biological source, at least in part, and other methanol may be derived from a petroleum source. The methanol is sent to a methanol to olefins reactor to produce a light olefin stream mainly comprising ethylene and propylene but with some impurities including higher molecular weight olefins, alkanes, carbon dioxide and hydrogen. The light olefin stream is treated in a light olefins recovery process in which the dried liquid and vapor olefin product is fractionated and sent to an oligomerization process and then to a hydrogenation section to produce the jet fuel as well as renewable diesel and naphtha streams. It has been found that the diesel and naphtha streams in addition to offgas streams and other waste streams may be sent to a steam reformer or autothermal reformer to produce hydrogen that can be used in the process.

[0028] 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 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.

[0001] The conversion of methanol to liquid fuel streams such as sustainable aviation fuel (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 synthesis unit, thereby increasing jet yield of a CO₂ to jet facility.

[0002] 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.

[0003] 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.

[0004] 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.

[0005] There are two alternatives to this approach:

[0006] (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.

[0007] (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.

[0008] 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.

[0009] 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).

[0010] 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 said 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 said 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 said alkane stream.

[0011] 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 said 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 said refined methanol stream with an MTO catalyst to produce a crude
5 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 said crude olefin stream by means of distillation to remove light ends into a
10 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 said one or more of said refined olefin streams with one or more oligomerization catalysts using one or more reaction vessels to produce a crude oligomerized
15 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 said crude oligomerized olefin stream by means of distillation to 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;
- 20 (g) reacting said refined oligomerized olefin stream with hydrogen with a hydrogenation catalyst to saturate the olefins to paraffins to create a crude jet fuel stream;
- (h) fractionating said 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
25 comprising jet fuel;
- (i) producing a recycle syngas stream comprising carbon oxides and hydrogen by
(1) reforming one or more of said 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 said waste gas streams; and
- 30 (j) co-feeding said recycle syngas stream to the methanol synthesis process of step A.

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.

[0012] 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 a an autothermal reactor to produce a third recycle syngas stream comprising CO and hydrogen.

[0013] The reaction of step (i) may also be 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.

[0014] 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.

[0015] 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.

[0016] 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 about 10 wt% and about 50 wt% propane. The reaction of step (i) may also be carried out using a dry reforming process.

The water electrolysis unit (electrolyzer) produces hydrogens and oxygen from water.

[0017] In the present disclosure, methanol is supplied to the process that may be made at a different site. The resultant methanol is then contacted with an MTO catalyst to produce an olefin stream. I

[0018] A block flow diagram shown in the Figure concerns the most relevant portions of the flow scheme 200 that provides hydrogen as needed to the process. An off-gas stream 202 is sent from several different columns including the oligomerization unit and the LORP unit to a pre-reforming section 205 with stream 210 sent to a steam methane reforming unit 215 with a flow of stream 204 sent to the pre-reforming section 205 and steam methane reforming unit 215. A portion 220 of the off-gas may be used to provide fuel in line 225 to steam methane reforming unit 225 and line 270 to be separated in pressure swing adsorption unit 250 to provide hydrogen 260. In addition, a hydrogen-rich off-gas stream 250 is added to the effluent 245 of the water gas shift unit 235.

[0019] The off-gas from columns 202 is the net overhead vapor streams from the several process units not shown in the figure including a demethanizer, depropanizer, flash stripper, and jet fractionator. The depropanizer off-gas would be the best candidate as feed and the flash stripper or demethanizer off-gas would be the best candidate to go to the pressure swing adsorption unit. Pre-reforming takes components in the feed gas that are heavier than methane and breaks them down to methane. This protects the steam methane reforming (SMR) reactor from excessive coking. SMR uses a catalyst at very high temperatures to convert methane and water to syngas (a mixture of carbon monoxide and hydrogen). This is a highly endothermic reaction so it requires an external fuel stream to provide the heat of reaction.

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10 Water gas shift reaction is at much lower temperatures. This shift reacts CO with additional water to create CO₂ and additional hydrogen. It is a mildly exothermic reaction. In the pressure swing adsorption process are treated the products from the water gas shift reactor that have a mix of hydrogen, CO₂, CO, and unconverted methane. The PSA product gas is high purity hydrogen and the tail gas contains the CO₂, CO, and unconverted methane, which is used as fuel for the

15 SMR reactor.

[0020] If the CO and unconverted methane from the PSA is insufficient to provide the necessary heat of reaction in the SMR, then additional fuel gas can be supplied from the off-gas from the columns. If the off-gas is hydrogen rich, then it will be routed to the PSA to recover hydrogen. If the off-gas is not hydrogen rich, then it would go directly to the SMR reactor as

20 fuel.

SPECIFIC EMBODIMENTS

[0021] 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.

[0022] A first embodiment of the invention is A process for providing hydrogen in a process

25 to produce jet fuel from methanol comprising sending an off-gas stream to a reforming section to produce a gas stream, sending a hydrogen-rich off-gas stream to be combined with said gas stream to provide a hydrogen enhanced gas stream and purifying said hydrogen enhanced gas stream to produce a hydrogen stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein

30 wherein said off-gas stream is first sent to a pre-reforming reactor within said reforming section

and then to a water gas shift reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein after passing through the water gas shift reactor, a gas stream is sent to a pressure swing adsorption unit to produce a stream of hydrogen. An embodiment of the invention is one, any or all of prior

5 embodiments in this paragraph up through the first embodiment in this paragraph wherein said off-gas stream is sent from at least one column selected from a demethanizer, depropanizer, flash stripper or jet fractionator or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said pressure swing adsorption unit treats a mixture of hydrogen, carbon dioxide, carbon

10 monoxide and unconverted methane. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said pressure swing adsorption unit produces a tail gas stream comprising carbon dioxide, carbon monoxide and unconverted methane. An embodiment of the invention is one, any or all of prior

15 embodiments in this paragraph up through the first embodiment in this paragraph wherein a portion of said off-gas stream is sent to supplement a fuel supply to a steam methane reforming reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said tail gas stream is sent to a steam reforming reactor as fuel gas. An embodiment of the invention is one, any or all of

20 prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said off-gas stream contains at least 10 mol% hydrogen. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said off-gas stream contains at least 20 mol% hydrogen. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

25 embodiment in this paragraph wherein said hydrogen stream is at least 95 mol% hydrogen. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein said hydrogen stream is at least 98 mol% hydrogen. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph 1 further comprising a control unit to measure the hydrogen concentration in said off-gas stream and then send an off-gas stream

30 containing an off-gas stream containing a hydrogen concentration below a predetermined value

to said reforming section as fuel gas and sending said off-gas stream to a pressure swing adsorption unit when the hydrogen concentration is above said predetermined level.

CLAIMS

1. A process for providing hydrogen in a process to produce jet fuel from methanol, comprising:
- 5 sending a hydrocarbon rich off-gas stream to a reforming reactor or a partial oxidation reactor to produce a gas stream;
- sending a hydrogen rich off-gas stream to be combined with said gas stream to provide a hydrogen enhanced gas stream; and
- purifying said hydrogen enhanced gas stream to produce a hydrogen stream.
2. The process of claim 1, wherein said off-gas stream is first sent to a pre-reforming
- 10 reactor and then to a water gas shift reactor.
3. The process of claim 2, wherein after passing through the water gas shift reactor, said gas stream is sent to a pressure swing adsorption unit to purify said hydrogen enhanced gas stream.
4. The process of claim 1, wherein said hydrocarbon rich off-gas stream is from at
- 15 least one column selected from a dealkanizer column and a jet fractionator column or combinations thereof.
5. The process of claim 1, wherein said hydrogen rich off-gas stream is from at least one column selected from a demethanizer column and a stripper column or combinations thereof.
6. The process of claim 3, wherein said pressure swing adsorption unit treats a
- 20 mixture of hydrogen, carbon dioxide, carbon monoxide and unconverted methane to produce said hydrogen stream.
7. The process of claim 3, wherein said pressure swing adsorption unit produces a tail gas stream comprising carbon dioxide, carbon monoxide and unconverted methane.
8. The process of claim 1, wherein a portion of said hydrocarbon rich off-gas stream
- 25 is sent to supplement a fuel supply to a reforming reactor or a partial oxidation reactor.
9. The process of claim 7, wherein said tail gas stream is sent to a steam reforming reactor or a partial oxidation reactor as fuel gas.
10. The process of claim 1 wherein said hydrocarbon rich gas stream is sent to a water gas shift reactor after said reforming reactor or said partial oxidation reactor.

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