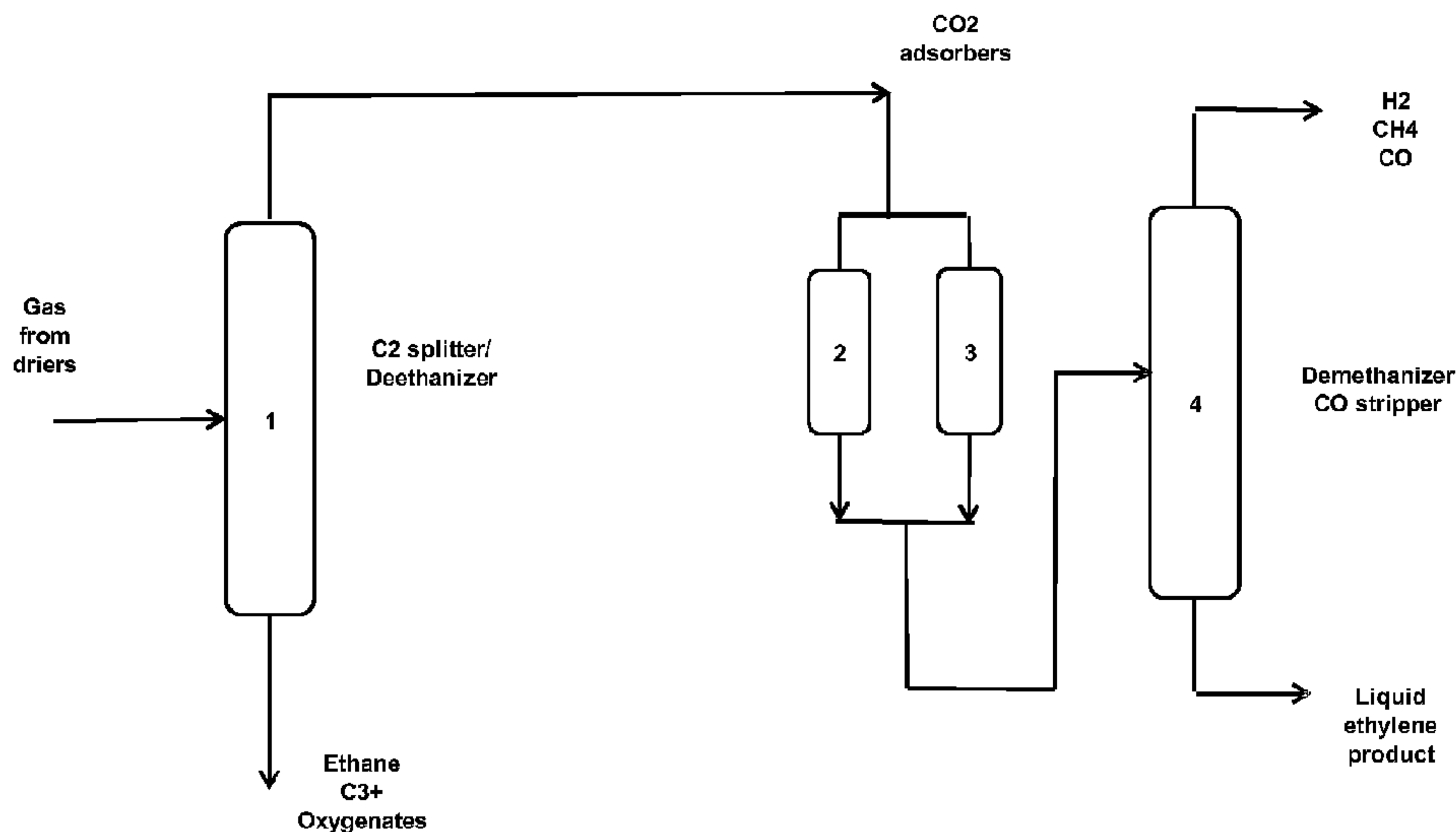




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(54) Title: PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM



(57) **Abrégé/Abstract:**

The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising : a)providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃₊ hydrocarbons, b)sending said stream (A) to a C₂ splitter/deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃₊ hydrocarbons, an overhead comprising the remaining components, c)sending said overhead to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, d)sending said stream essentially free of CO₂ to a demethanizer/CO stripper to recover an overhead comprising H₂, CH₄ and CO, liquid ethylene at the bottoms. In another embodiment the CO₂ removal step can be made on the recovered ethylene.

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(54) Title: PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM

(57) Abstract: The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising : a)providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons, b)sending said stream (A) to a C₂ splitter/deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead comprising the remaining components, c)sending said overhead to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, d)sending said stream essentially free of CO₂ to a demethanizer/CO stripper to recover an overhead comprising H₂, CH₄ and CO, liquid ethylene at the bottoms. In another embodiment the CO₂ removal step can be made on the recovered ethylene.

WO 2013/014003 A1

PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM

5 [Field of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream.

Olefins are traditionally produced from petroleum feedstocks by catalytic
10 or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s), such as ethylene and/or propylene, from a variety of hydrocarbon feedstock. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds. The limited supply and increasing cost of crude
15 oil has prompted the search for alternative processes for producing hydrocarbon products.

Olefins can be produced by dehydration of the corresponding alcohol. Ethanol can be obtained by fermentation of carbohydrates. Made up of organic matter from living organisms, biomass is the world's leading renewable energy
20 source. The effluent produced by the ethanol dehydration comprises essentially unconverted ethanol, water, ethylene, acetaldehyde. Acetaldehyde may cause problems in ethylene recovery operations. It may comprise also very small amounts of ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons. The weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene is most of
25 time less than 20/80.

[Background of the invention]

US 20030098281 A1 describes a method of controlling water and/or
30 oxygenate concentrations of an olefin stream. The method includes contacting the olefin stream with a liquid absorbent. The liquid absorbent is selected from the group consisting of a polyol, amine, amide, nitrile, heterocyclic nitrogen

containing compound, and mixtures thereof. A gaseous stream comprising essentially steam, ethylene, propylene and less than 2 w% of oxygenates is condensed in a quench tower. The overhead of said quench tower is washed with a caustic solution to remove CO₂ and then contacted with the liquid
5 absorbent to remove the oxygenates.

WO 03 020670 A1 provides a method for removing oxygenated components such as acetaldehyde, CO₂ and/or water from an olefin stream. It explains it is desirable to remove such oxygenated components, since they may
10 poison catalysts that are used to further process olefin composition. In addition, the presence of certain oxygenated compounds, such as acetaldehyde, can cause fouling in other olefin purification units, e.g., acid gas treating units. The method comprises providing an olefin stream containing ethylene, propylene, C₄+ olefins and acetaldehyde. The olefin stream is separated into a first fraction
15 and a second fraction, wherein the first fraction comprises at least a majority of the ethylene and/or propylene present in the olefin stream, and the second fraction comprises at least a majority of the C₄+ olefins and acetaldehyde present in the olefin stream. The first fraction is then acid gas treated by sodium hydroxide or potassium hydroxide. The olefin stream is separated by distillation,
20 preferably, the distillation is extractive distillation using an extractant. The preferred extractant is a polar composition having an average boiling point of at least 38°C at 1 atm. Methanol is one type of preferred extractant.

WO 03 020672 A1 describes method of removing dimethyl ether from an
25 ethylene and/or propylene containing stream. The olefin stream is passed to a water absorption column, methanol is used as the water absorbent. Methanol and entrained water, as well as some oxygenated hydrocarbon, is recovered as the bottoms stream of said water absorption column, an overhead olefin is recovered and sent to a distillation column. The distillation column separates
30 ethylene and propylene, as well as lighter boiling point components from the dimethyl ether and heavier boiling point components, including C₄+ components and methanol remaining from the methanol wash. Additional

methanol is added to the distillation column to reduce clathrate and/or free water formation in the distillation column. The ethylene and propylene containing stream exits the distillation column as overhead and the heavier boiling point components which include the dimethyl ether and C4+ components exit the distillation column as the bottoms. Ethylene and propylene then flow to a caustic wash column.

WO 03 033438 A1 describes a method for processing an olefin stream containing oxygenates and water, comprising: providing an olefin stream containing oxygenates and water; dewatering the olefin stream; compressing the dewatered olefin stream; washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream; contacting the methanol washed olefin stream with water; and fractionating the water contacted olefin stream. The recovered olefin stream (washed with methanol and then with water) is further sent to an alkali wash and a drying step. The olefin stream containing oxygenates and water is the effluent of an MTO process.

US 6,444,869 describes a process for the production of ethylene from an oxygenate conversion effluent stream. The oxygenate conversion effluent stream comprises hydrogen, methane, ethylene, ethane, propylene, propane and C4+ olefins. This effluent is compressed, treated to remove oxygenates, passed to a carbon dioxide removal zone wherein carbon dioxide is absorbed by contacting a caustic solution or by contacting an amine solution in combination with a caustic solution in a conventional manner to remove the carbon dioxide, dried, then fractionation is made through a deethanizer and a demethanizer.

US 2005-0283038 A1 described a process for producing an olefins stream from a first vapor effluent stream from an oxygenate to olefin conversion reaction, said first vapor effluent stream comprising C2 and C3 olefins, C4 hydrocarbons, and C2 to C6 carbonyl compounds. In the process, the

temperature and pressure of the first vapor effluent stream are adjusted to produce a second vapor effluent stream having a pressure ranging from about 100 psig to about 350 psig (790 to 2514 kPa) and a temperature ranging from about 70° F. to about 120° F. (21 to 49° C.), said second vapor effluent stream
5 containing about 50 wt. % or more C4 hydrocarbons based upon the total weight of C4 hydrocarbons in the first vapor effluent stream. The second vapor effluent stream is then washed with a liquid alcohol-containing stream to produce a third vapor effluent stream, whereafter the third vapor effluent stream is washed with liquid water to provide a fourth vapor effluent stream comprising
10 the C2 and C3 olefins and about 1.0 wt. % or less C2 to C6 carbonyl compounds. In one embodiment of such a recovery process, at least part of the fourth vapor effluent stream is contacted with a basic component, such as caustic or an amine, to remove the bulk of the carbon dioxide therefrom (thus removing "acid gas" from the fourth vapor effluent stream), whereafter the CO₂-
15 depleted stream is dried.

The main drawback of the above prior arts is the fouling of the caustic scrubber. The inlet gas to the caustic scrubber contains reactive oxygenates like aldehydes and ketones. These aldehydes react in the aldol condensation
20 reaction in the caustic tower environment to form significant red oil polymers. This causes significant fouling concerns in the caustic tower which impact the unit run length. The spent caustic treatment with significant red oil polymer content is also an important concern as well as the spent caustic treatment and disposal issues. In addition there are the handling and disposal issues of red oil
25 polymers.

It has now been discovered a process for removing oxygenated contaminants from an ethylene stream wherein there is no caustic wash to remove the CO₂ and no wash column to remove the oxygenates. Oxygenates
30 are organic compounds consisting of carbon, oxygen and hydrogen.

[Brief summary of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

- a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons,
- b) sending said stream (A) to a C₂ splitter/deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead comprising the remaining components,
- c) sending said overhead to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂,
- d) sending said stream essentially free of CO₂ to a demethanizer/CO stripper to recover an overhead comprising H₂, CH₄ and CO, liquid ethylene at the bottoms.

15

In another embodiment the CO₂ removal step can be made on the recovered ethylene. In said embodiment the present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

- a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons,
- b1) sending said stream (A) to a C₂ splitter/deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead comprising the remaining components,
- c1) sending said overhead stream to a demethanizer/CO stripper to recover an overhead comprising H₂, CH₄ and CO, liquid ethylene comprising CO₂ at the bottoms.
- d1) sending said ethylene comprising CO₂ to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

30

In an embodiment the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 10/90.

In an embodiment the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

5 In an embodiment the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 5/95.

In an embodiment the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

10 In an embodiment the proportion of oxygenates in (A) is up to 3000 wppm.

In an embodiment the proportion of oxygenates in (A) is up to 2000 wppm.

In an embodiment the proportion of H₂ in (A) is from 5 to 1000 wppm.

15 In an embodiment the proportion of H₂ in (A) is up to 800 wppm.

In an embodiment the proportion of H₂ in (A) is up to 500 wppm.

20 Advantageously "dried ethylene stream" at step a) means a water content less than 5 wppm, advantageously less than 3wppm and preferably less than 1 wppm.

In an embodiment when the dried ethylene stream (A) has been made by ethanol dehydration said stream (A) contains substantially no acetylene.

25 Ethylene treated in accordance with this invention is particularly suitable for use as feedstock for making alpha-olefins, ethylbenzene/styrene, ethyleneoxide/ethyleneglycol, ethylenedichloride and corresponding polymers, like polyethylene homo or copolymer (PE, EPR, EPDM etc), polystyrene (PS), styrene copolymers with butadiene, isoprene, acrylonitrile or combinations
30 (SBS, SIS, SBR, ABS, SAN), polyesters (PET) and polyvinylchlorides (PVC)

[Detailed description of the invention]

As regards the oxygenated contaminants, also referred to as oxygenates, one can cite ethanol, C3 alcohols; ethers such as diethylether and methyl ethyl ether; carboxylic acids such as acetic acid; aldehydes such as acetaldehyde; ketones such as acetone; and esters such as methyl esters.

- 5 Particularly problematic oxygenate contaminants in an alcohol dehydration are aldehydes.

As regards the ethylene stream (A) of step a), it can be originating
10 from the dehydration of ethanol. Said dehydration can be made in one or more ethanol dehydration reactors. As regards alcohol dehydration, such process is described in WO-2009-098262, WO-2009-098267, WO-2009-098268 and WO-2009-098269. The present invention is very efficient for the purification of ethylene produced by dehydration of ethanol.

15

The outlet of said dehydration reactor comprises essentially ethylene and steam as well as minor amounts of oxygenates, ethane, CO, O₂, H₂, CH₄ and C₃+ hydrocarbons. "Minor amounts" means the weight ratio of +C₃+ hydrocarbons to ethylene is less than 20/80 and most of time less than 10/90.

20

Said outlet of dehydration reactor is initially cooled, typically in a quench tower employing water as the quench medium. In the quench tower, most of the water contained in the outlet of dehydration reactor is condensed and is removed from the bottom of the tower as a liquid water bottom stream. A part of said water
25 bottom stream is cooled in a heat exchanger and recycled as quenching medium to the top of the quench column. The part of the water bottom stream which is not recycled as quenching medium may contain a part of the oxygenates and mostly unconverted ethanol if any. Said stream can be treated in a stripping column to recover a pure water stream. Ethylene, oxygenates,
30 ethane, CO, O₂, H₂, CH₄ and C₃+ hydrocarbons are removed from the top of the quench tower at a pressure typically such as 1 to 16 bars absolute and are referred to as the contaminated ethylene stream.

Advantageously said contaminated ethylene stream is successively compressed and cooled in one or more steps to remove the major part of water, further fed to a fixed bed drying zone and finally to the C2 splitter/deethanizer of step b).

5 In the previous compression steps the recovered water contains a part of the oxygenated contaminants and hydrocarbons dissolved. The contaminated hydrocarbon stream can also be cooled before the first compression step and water recovered. In an embodiment the water recovered upon each cooling further to a compression step and upon cooling, if any, before the first
10 compression step is sent to a stripping column to produce an overhead stream comprising essentially oxygenated contaminants and hydrocarbons and an essentially pure water bottoms stream. Optionally the overhead stream is burned to destroy the oxygenated contaminants and recover heat.

15 After the compression steps the contaminated ethylene stream is further fed to a fixed bed drying zone and finally to the C2 splitter/deethanizer of step b). The fixed bed drying zone is known in itself.

As regards the C2 splitter/deethanizer of step b), it is advantageously
20 a distillation column. The overhead is a mixture of ethylene, CO, CO₂, H₂ and CH₄.

As regards the fixed bed CO₂ adsorption zone of step c), it can be any component capable to selectively remove CO₂. By way of example it is an
25 available commercial fixed bed adsorption (PSA for pressure swing adsorption or TSA for temperature swing adsorption) using molecular sieves or basic oxides, supported basic oxides, high surface area carbons, organo-metallic framework components (MOF's) or mixture thereof. The molecular sieves are preferably low silica zeolites, having 8 (among which zeolite A) or 12 membered
30 (among which zeolite X) rings and exchanged with alkali, alkaline earth or lanthanide cations. Other molecular sieves are crystalline titanosilicates (ETS family materials). Supported basic oxides are preferably, alkali, alkaline earth or

lanthanide oxides supported on high surface area carbons, alumina, silica, zirconia or titania. The removal of CO₂ can be carried out with a liquid stream or with a gaseous ethylene stream depending on the pressure and temperature. A stream essentially free of CO₂ is recovered. As only trace amounts of CO₂ have to be removed from the ethylene, the preferred process cycle is of the thermal swing adsorption (TSA) type. Said fixed bed adsorbent, once saturated with CO₂, can be regenerated, during regeneration the desorption produces a stream which can be treated anywhere. In a TSA process cycle, the regeneration is done while sweeping the saturated adsorbent with an inert gas by increasing the temperature until desorption of the CO₂ occurs. Eventually the saturated adsorbent can be replaced by new adsorbent and the saturated adsorbent either be disposed of or regenerated ex-situ for further use. "Essentially" has to be interpreted in the light of the further use of ethylene. Should ethylene to be polymerized CO₂ has to be 1 ppm vol or less and preferably 0.5 ppm vol or less.

As regards the demethanizer, purpose is to recover an overhead comprising H₂, CH₄ and CO and liquid ethylene at the bottoms. It is advantageously a distillation column.

20

As regards the operating conditions, The demethanizer of step d) has to be at a pressure high enough to operate at temperatures which are not too low. A demethanizer to recover an overhead comprising H₂, CH₄ and CO and liquid ethylene at the bottoms operating at 40 barg has an overhead temperature of around 0 to -10°C and a bottom temperature of around 0°C. The same demethanizer operating at 21 barg has an overhead temperature of -30°C and a bottom temperature of around -24°C.

These temperatures and pressures are a function of the proportion of H₂, CH₄ and CO in the ethylene stream (A) and mainly of the proportion of H₂. The proportion of H₂, CH₄ and CO in the ethylene stream (A) and mainly the proportion of H₂ governs also the pressure and temperature of the C₂ splitter/deethanizer located upstream said demethanizer.

30

In an embodiment the pressure of step b) is selected to have a temperature of the C2 splitter/deethanizer bottoms such as there is no oligomerization or polymerization of the oxygenates. By way of example said temperature should not exceed 150°C and advantageously not exceed 100°C. This temperature is function of the pressure and of the proportion of oxygenates in the mixture of oxygenates+ethane+C3+ hydrocarbons. The higher the proportion of oxygenates the higher the temperature. The higher the pressure the higher the temperature.

10

In an embodiment the C2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C2 splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to four compression stages in series (depending on dehydration reactor pressure), sent to the driers and finally to the C2 splitter deethanizer.

Said embodiment is described on fig 1 wherein (1) is the C2 splitter deethanizer, (2) and (3) the CO₂ adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons and an overhead comprising ethylene, CO, CO₂, H₂ and CH₄ (condenser, decanter and reflux of C2 splitter deethanizer are not shown, reboiler of C2 splitter deethanizer is not shown). Said overhead is sent to the CO₂ adsorbers (2) and (3) to recover a stream essentially free of CO₂ and then to the demethanizer/CO stripper (4) to recover an overhead comprising H₂, CH₄ and CO and liquid ethylene at the bottoms. Condenser, decanter and reflux of the demethanizer/CO stripper are not shown, reboiler of the demethanizer/CO stripper is not shown.

In a specific example according to fig 1 the pressure of the C2 splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -20°C to -30°C, condensed at a temperature in the range -20°C to -30°C, the temperature on bottoms of said splitter/deethanizer is
5 around 70 to 90°C, the pressure of the demethanizer/CO stripper around 15 to 25 barg, the top of the demethanizer/CO stripper is around -15°C to -35°C, is condensed at a temperature around -15 to -35°C and the temperature on bottoms of the demethanizer/CO stripper is around -15°C to -35°C.

Advantageously the pressure of the C2 splitter/deethanizer is around 18
10 to 25 barg, the top of said splitter/deethanizer is at a temperature around -18°C to -28°C, condensed at a temperature in the range -18°C to -28°C, the temperature on bottoms of said splitter/deethanizer is around 75 to 85°C, the pressure of the demethanizer/CO stripper around 18 to 25 barg, the top of the demethanizer/CO stripper is around -20°C to -30°C, is condensed at a
15 temperature around -20 to -30°C and the temperature on bottoms of the demethanizer/CO stripper is around -20°C to -30°C.

In an embodiment the pressure of the C2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the
20 pressure of the C2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C2 splitter /deethanizer is ranging from 10 to 25 barg In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to three compression stages in series,
25 sent to the driers and finally to the C2 splitter deethanizer. Then the overhead of the C2 splitter deethanizer is compressed and sent through the CO2 adsorbers to the demethanizer/CO stripper. Optionally the essentially CO2 free stream leaving the fixed bed CO2 adsorption zone is cooled, sent to a decanter to produce a liquid phase sent as a reflux to the C2 splitter/deethanizer and a
30 gaseous phase sent to the demethanizer/CO stripper.

Said embodiment is described on fig 2. The contaminated ethylene stream from the quench column has been dried and sent at a pressure around

15 to 25 barg to the C2 splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO₂, H₂ and CH₄. Said overhead (top of the the C2 splitter deethanizer) is sent to the compressor
5 (6) to increase the pressure with 10 to 25 barg over the C2 splitter /deethanizer pressure, optionally cooled (the cooler is not shown) and sent to the CO₂ adsorbers (2) and (3) to recover a stream essentially free of CO₂. Then said CO₂ free stream is cooled (the cooler is not shown) and sent to the decanter (5) to produce a liquid phase sent as a reflux to the C2 splitter deethanizer (1) and
10 a gaseous phase sent to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead (the condenser, decanter and reflux are not shown) comprising H₂, CH₄ and CO and liquid ethylene at the bottoms (the reboiler is not shown).

Alternatively, the condenser and decanter (5) can be installed between
15 the top outlet of the C2 splitter/deethaniser (1) and the compressor (6). The produced liquid phase is sent as a reflux to the C2 splitter/deethaniser (1) while the gaseous phase is sent to the compressor (6). In other words the contaminated ethylene stream from the quench column has been dried and sent to the C2 splitter deethanizer (1) to produce a bottom stream comprising
20 essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO₂, H₂ and CH₄ Said overhead, the top outlet of the C2 splitter/deethaniser (1), is condensed, sent to a decanter to get a liquid phase sent as a reflux to the C2 splitter/deethaniser (1) and a gaseous phase sent to the compressor (6). Then the compressed stream is sent to the CO₂
25 adsorbers (2) and (3) to recover a stream essentially free of CO₂ and then to the demethanizer/CO stripper (4) to recover an overhead comprising H₂, CH₄ and CO and liquid ethylene at the bottoms.

In a specific example according to fig 2 the pressure of the splitter/deethanizer is around 15 to 25 barg, the temperature on top of said
30 splitter/deethanizer around -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is around

-10°C to 10°C, is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the temperature on top of said splitter/deethanizer around -28°C to -32°C, the temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is around -5°C to 5°C, is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

10

As regards the other embodiment wherein the CO₂ removal step is made on the recovered ethylene, it works in a similar way as explained above in which the CO₂ removal step is before the demethanizer/CO stripper.

In an embodiment the C₂ splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C₂ splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to four compression stages in series (depending on dehydration reactor pressure), sent to the driers and finally to the C₂ splitter deethanizer.

Said embodiment is described on fig 3 wherein (1) is the C₂ splitter deethanizer, (2) and (3) the CO₂ adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C₂ splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C₃+ hydrocarbons and an overhead (the condenser, the decanter and the reflux are not shown) comprising ethylene, CO, CO₂, H₂ and CH₄. Said overhead is sent the demethanizer/CO stripper (4) to recover an overhead (the condenser, the decanter and the reflux are not shown) comprising H₂, CH₄ and CO and liquid ethylene comprising CO₂ at the bottoms (the reboiler is not shown). Said

ethylene comprising CO₂ is sent to a fixed bed CO₂ adsorption zone, the CO₂ adsorbers (2) and (3) to recover an ethylene stream essentially free of CO₂.

In a specific example according to fig 3 the pressure of the C₂ splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -20°C to -30°C, condensed at a temperature in the range -20°C to -30°C, the temperature on bottoms of said splitter/deethanizer is around 70 to 90°C, the pressure of the demethanizer/CO stripper around 15 to 25 barg, the top of the demethanizer/CO stripper is around -15°C to -35°C, is condensed at a temperature around -15 to -35°C and the temperature on bottoms of the demethanizer/CO stripper is around -15°C to -35°C.

Advantageously the pressure of the C₂ splitter/deethanizer is around 18 to 25 barg, the top of said splitter/deethanizer is at a temperature around -18°C to -28°C, condensed at a temperature in the range -18°C to -28°C, the temperature on bottoms of said splitter/deethanizer is around 75 to 85°C, the pressure of the demethanizer/CO stripper around 18 to 25 barg, the top of the demethanizer/CO stripper is around -20°C to -30°C, is condensed at a temperature around -20 to -30°C and the temperature on bottoms of the demethanizer/CO stripper is around -20°C to -30°C.

In an embodiment the pressure of the C₂ splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the pressure of the C₂ splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C₂ splitter /deethanizer is ranging from 10 to 25 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to three compression stages in series, sent to the driers and finally to the C₂ splitter deethanizer. Then the overhead of the C₂ splitter deethanizer is compressed and sent to the demethanizer/CO stripper.

Said embodiment is described on fig 4. In addition to fig 3 there are additional equipment : a compressor (6). The contaminated ethylene stream

from the quench column has been dried and sent at a pressure around 15 to 25 barg to the C2 splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO₂, H₂ and CH₄. Said overhead is condensed, sent to a decanter to get a liquid phase sent as a reflux to (1) and a gaseous phase sent to the compressor (6). Said condenser, decanter and reflux are not shown). The compressor (6) increases the pressure with 10 to 25 barg over the C2 splitter /deethanizer pressure, and the compressed stream is sent to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead (the condenser, the decanter and the reflux are not shown) comprising H₂, CH₄ and CO and at the bottom liquid ethylene comprising CO₂ (the reboiler is not shown). Said ethylene comprising CO₂ is sent to a fixed bed CO₂ adsorption zone, the CO₂ adsorbers (2) and (3) to recover an ethylene stream essentially free of CO₂.

In a specific example according to fig 4 the pressure of the splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -25°C to -35°C, condensed at a temperature in the range -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer is around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is around -10°C to 10°C, is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the top of said splitter/deethanizer is at a temperature around -28°C to -32°C, the temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is around -5°C to 5°C, is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

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[Example]

The process according to fig 5 is operated. Fig 5 is derived from fig 2 by changing the position of the condenser and decanter (5), they are located between the outlet of the C2 splitter/deethaniser and the compressor. The results are on the following table.

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| stream No on fig 5 | | 1 | 2 | 3 |
|--------------------|-------|------------------|---------------------|-----------------------------|
| | | C2 splitter feed | C2 splitter bottoms | C2 splitter vapor distillat |
| Temperature | °C | 15 | 80 | -30 |
| Pressure | bar g | 20 | 19 | 19 |
| H2 | kg/h | 8 | | 8 |
| CO | kg/h | 1 | | 1 |
| CO2 | kg/h | 1 | | 1 |
| ethane | kg/h | 23 | 11 | 12 |
| ethylene | kg/h | 25108 | 30 | 25078 |
| acetaldehydes | kg/h | 150 | 150 | |
| C3+ | kg/h | 715 | 715 | |
| Total | kg/h | 26006 | 906 | 25100 |

| stream No on fig 5 | | 4 | 6 | 5 |
|--------------------|-------|-------------------|--------------------|------------------|
| | | Demethanizer feed | Demethanizer purge | Ethylene product |
| Temperature | °C | -2 | -40 | 20 |
| Pressure | bar g | 40 | 40 | 20 |
| H2 | kg/h | 8 | 8 | |
| CO | kg/h | 1 | 1 | |
| CO2 | kg/h | | | |
| ethane | kg/h | 12 | | 12 |
| ethylene | kg/h | 25078 | 90 | 24988 |
| acetaldehydes | kg/h | | | |
| C3+ | kg/h | | | |
| Total | kg/h | 25099 | 99 | 25000 |

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CLAIMS:

1. Process for removing oxygenated contaminants from an ethylene stream comprising :
 - a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons,
 - b) sending said stream (A) to a C₂ splitter/deethanizer to produce a first bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, and a first overhead stream comprising the remaining components,
 - c) sending said first overhead stream to a fixed bed CO₂ adsorption zone to recover a second overhead stream essentially free of CO₂,
 - d) sending said second overhead stream to a demethanizer/CO stripper to recover a third overhead stream comprising H₂, CH₄ and CO, and a second bottom stream comprising liquid ethylene .

2. Process according to claim 1 wherein the C₂ splitter /deethanizer and the demethanizer are operating at the same pressure, except the pressure drop between the C₂ splitter /deethanizer and the demethanizer for transfer of fluids, and said pressure is ranging from 15 to 45 barg.

3. Process according to claim 1 wherein the pressure of the C₂ splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C₂ splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C₂ splitter /deethanizer is ranging from 10 to 25 barg.

4. Process according to claim 3 wherein the first overhead stream is condensed, sent to a decanter to get a liquid phase which is sent as a reflux to said C₂ splitter/deethaniser and a gaseous phase sent to a compressor, then the compressed stream is sent to the CO₂ adsorption zone.

5. Process according to claim 3 wherein the first overhead stream is sent to a compressor, optionally cooled and sent to the CO₂ adsorption zone to recover the second overhead stream, then said second overhead stream is cooled and sent to a decanter to produce a liquid phase sent as a reflux to the C₂ splitter/deethanizer and a gaseous phase sent to the demethanizer/CO stripper.

6. Process for removing oxygenated contaminants from an ethylene stream comprising :

- a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons,
- b1) sending said stream (A) to a C₂ splitter/deethanizer to produce a first bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, and a first overhead stream comprising the remaining components,
- c1) sending said first overhead stream to a demethanizer/CO stripper to recover a second overhead stream comprising H₂, CH₄ and CO, and a second bottom stream comprising liquid ethylene and CO₂,
- d1) sending said second bottom stream to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

7. Process according to claim 6 wherein the C₂ splitter /deethanizer and the demethanizer are operating at the same pressure, except the pressure drop between the C₂ splitter /deethanizer and the demethanizer for transfer of fluids, and said pressure is ranging from 15 to 45 barg.

8. Process according to claim 6 wherein the pressure of the C₂ splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C₂ splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C₂ splitter /deethanizer is ranging from 10 to 25 barg.

9. Process according to any one of claims 6 to 8 wherein the first overhead stream is condensed, sent to a decanter to get a liquid phase sent as a reflux to said C2 splitter/deethaniser and a gaseous phase sent to a compressor, then the compressed stream is sent to the demethanizer/CO stripper.

10. Process according to any one of claims 1 to 9 wherein the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 10/90.

11. Process according to claim 10 wherein the weight ratio of ethane+CO+CO₂+H₂+CH₄-FC₃+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

12. Process according to any one of claims 1 to 9 or claim 11 wherein the weight ratio of ethane+CO+CO₂+H₂+CH₄-FC₃+ hydrocarbons to ethylene in (A) is less than 5/95.

13. Process according to any one of claims 1 to 12 wherein the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

14. Process according to any one of claims 1 to 13 wherein the proportion of oxygenates in (A) is up to 3000 wppm.

15. Process according to claim 14 wherein the proportion of oxygenates in (A) is up to 2000 wppm.

16. Process according to any one of claims 1 to 15 wherein the proportion of H₂ in (A) is from 5 to 1000 wppm.

17. Process according to any one of claims 1 to 16 wherein the proportion of H₂ in (A) is up to 800 wppm.

18. Process according to claim 17 wherein the proportion of H₂ in (A) is up to 500 wppm.

19. Process according to any one of claims 1 to 18 wherein the dried ethylene stream (A) is originating from the dehydration of ethanol.

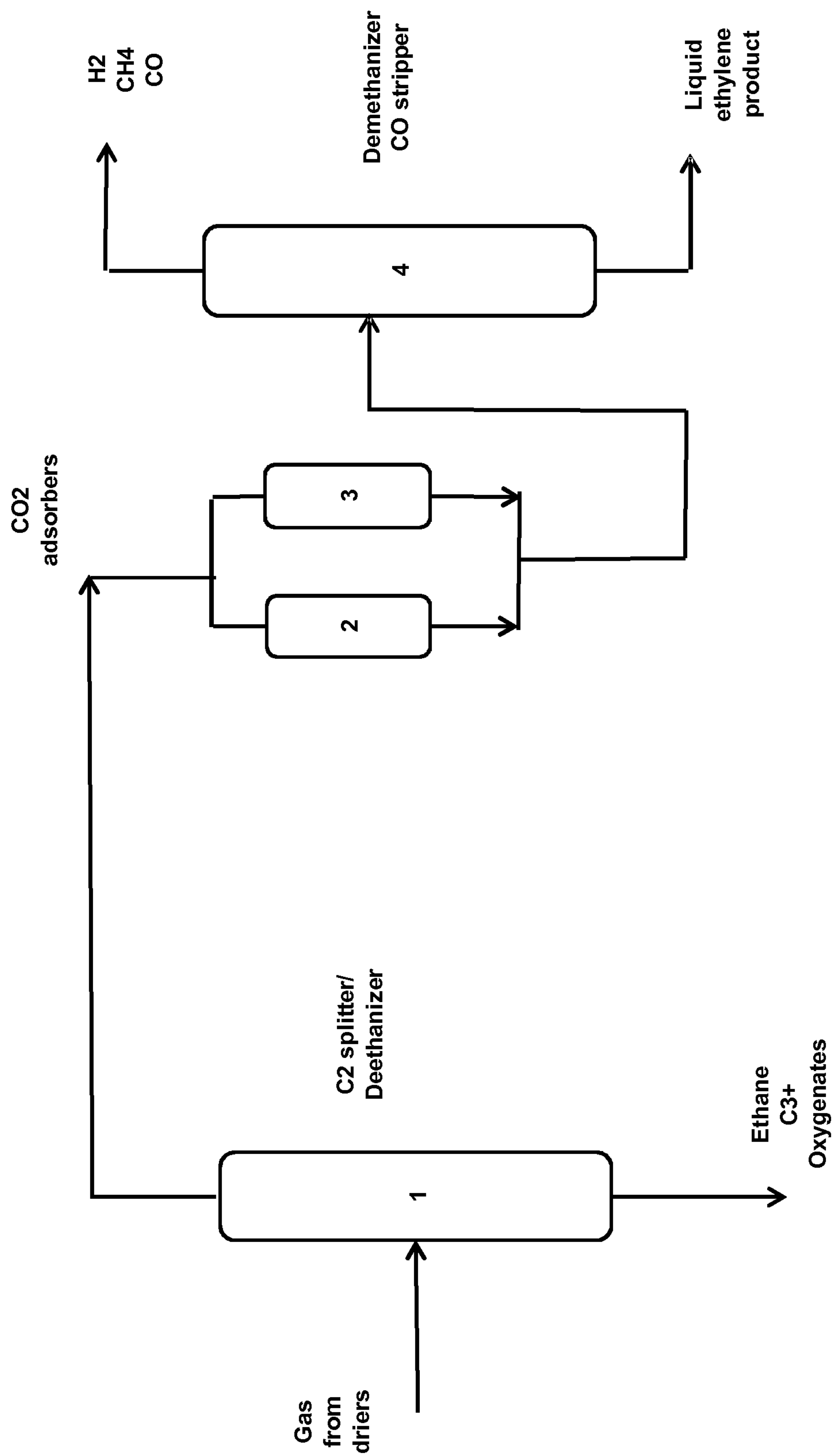


Fig 1

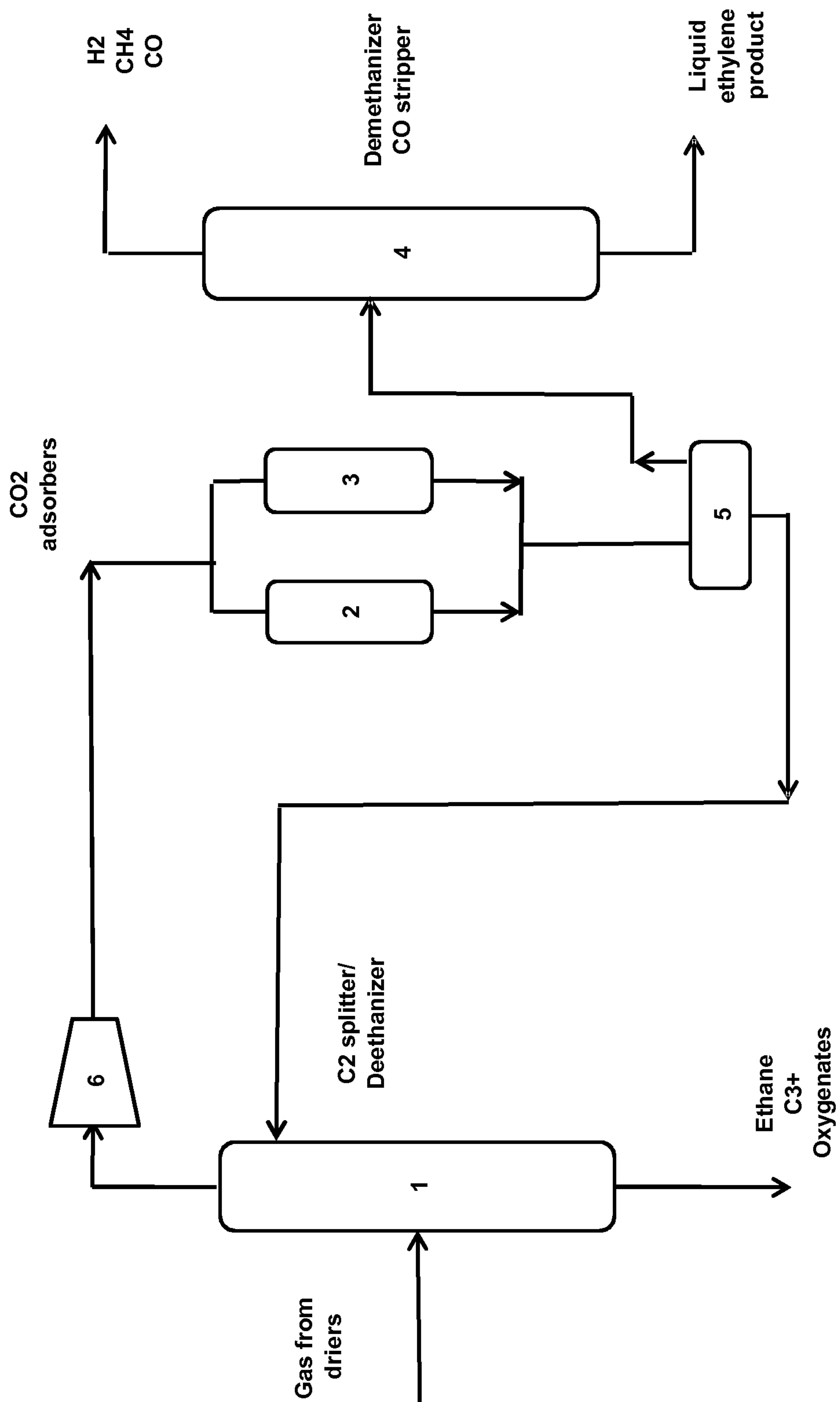


Fig 2

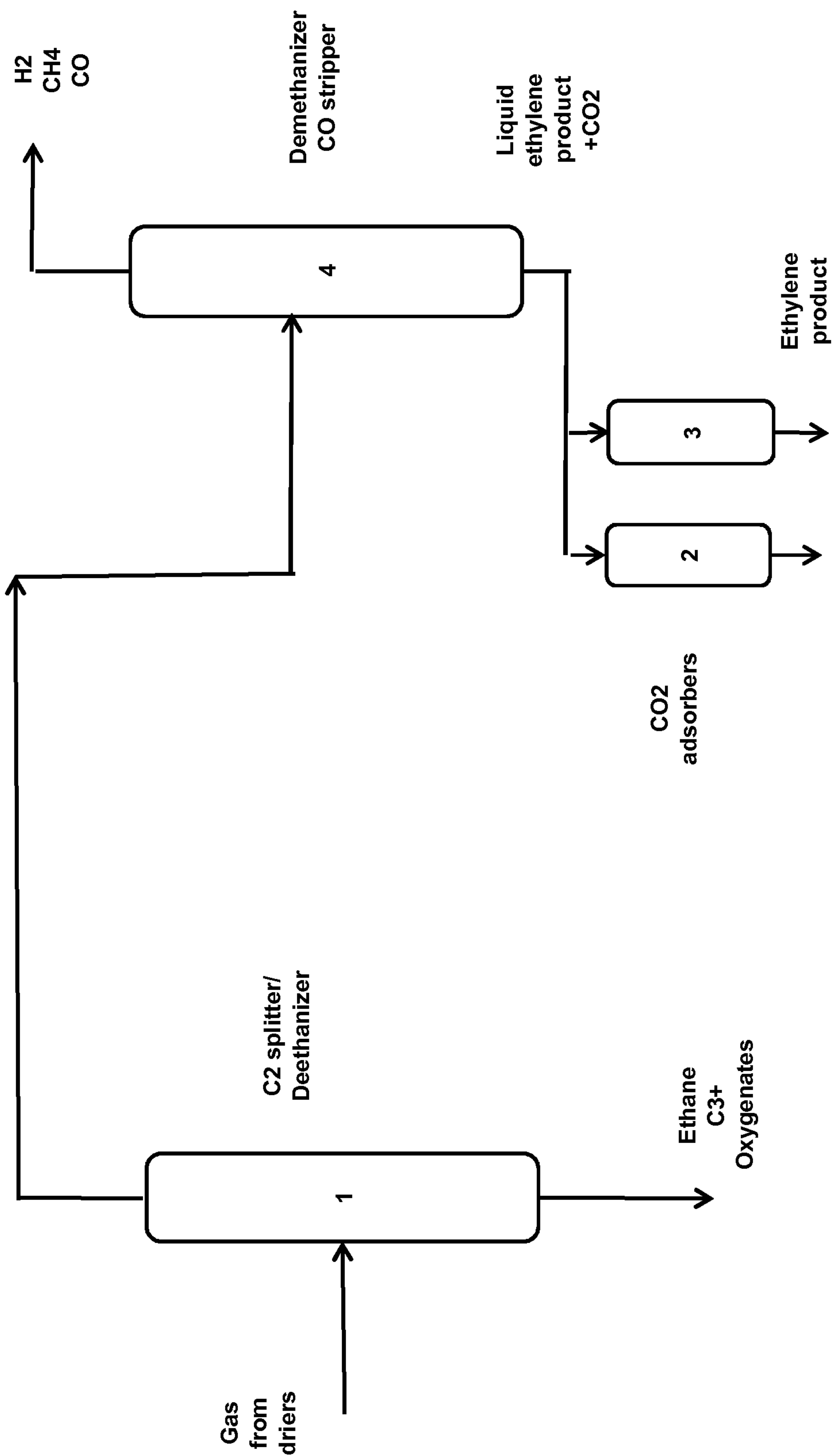


Fig 3

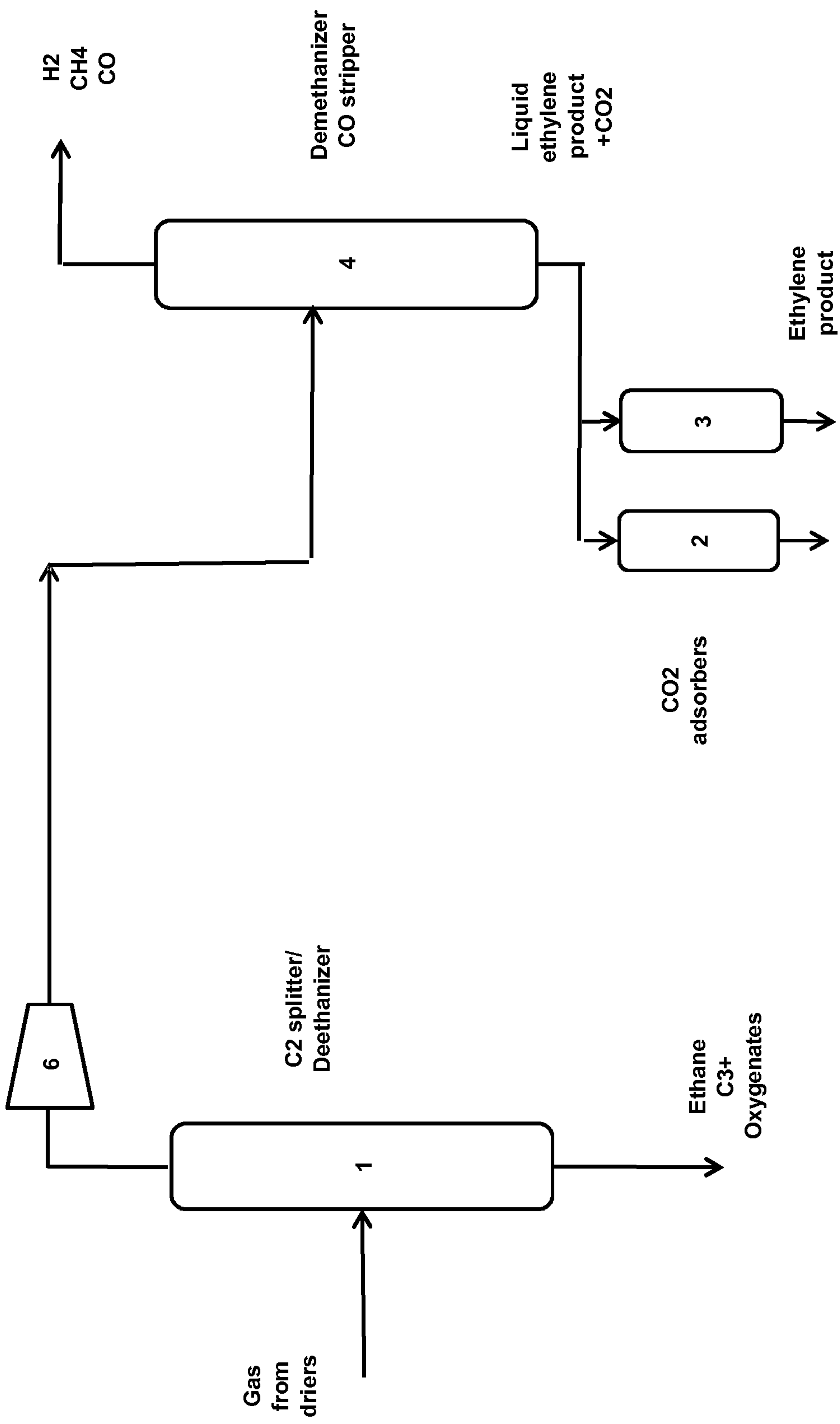


Fig 4

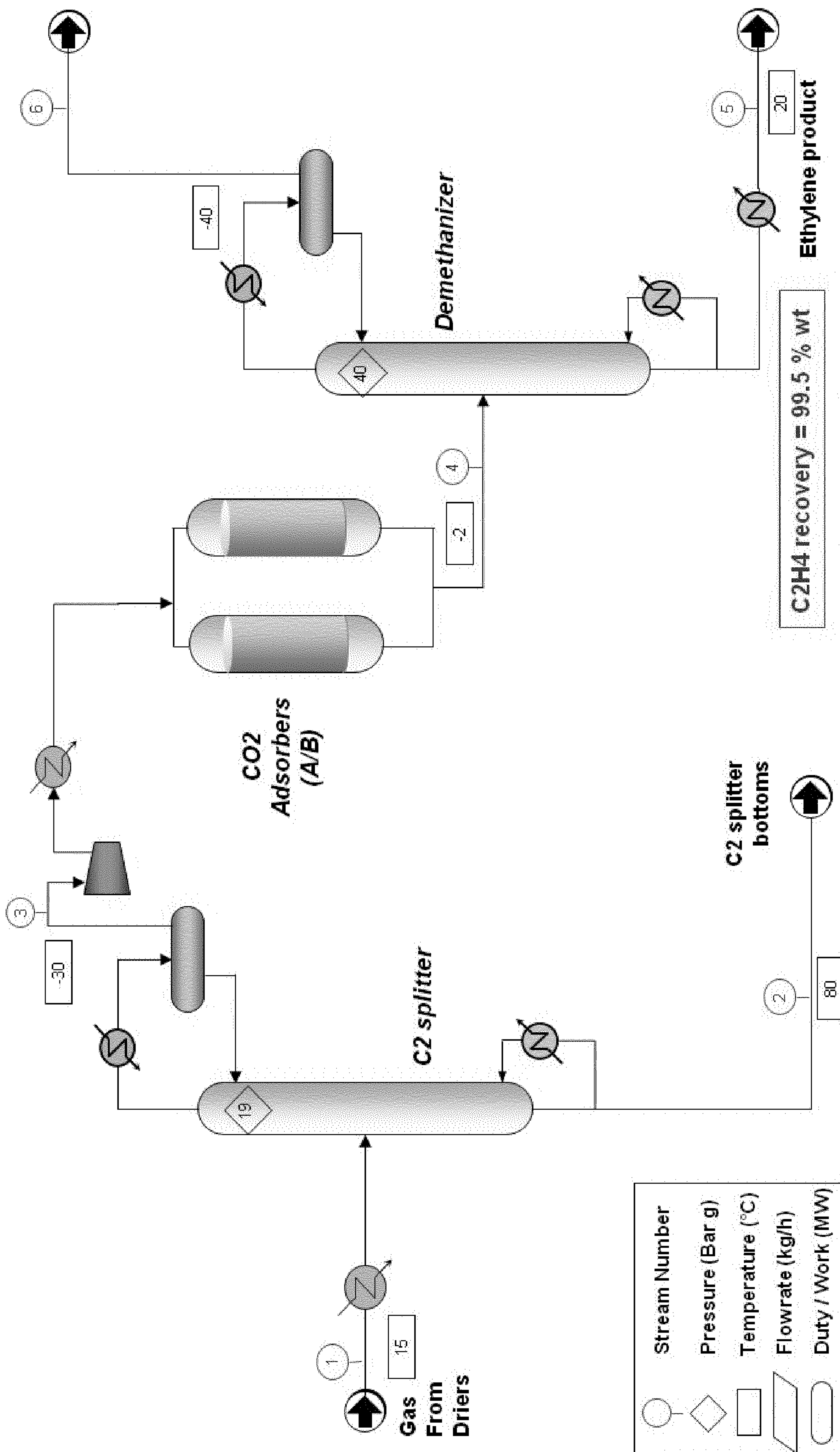


Fig 5

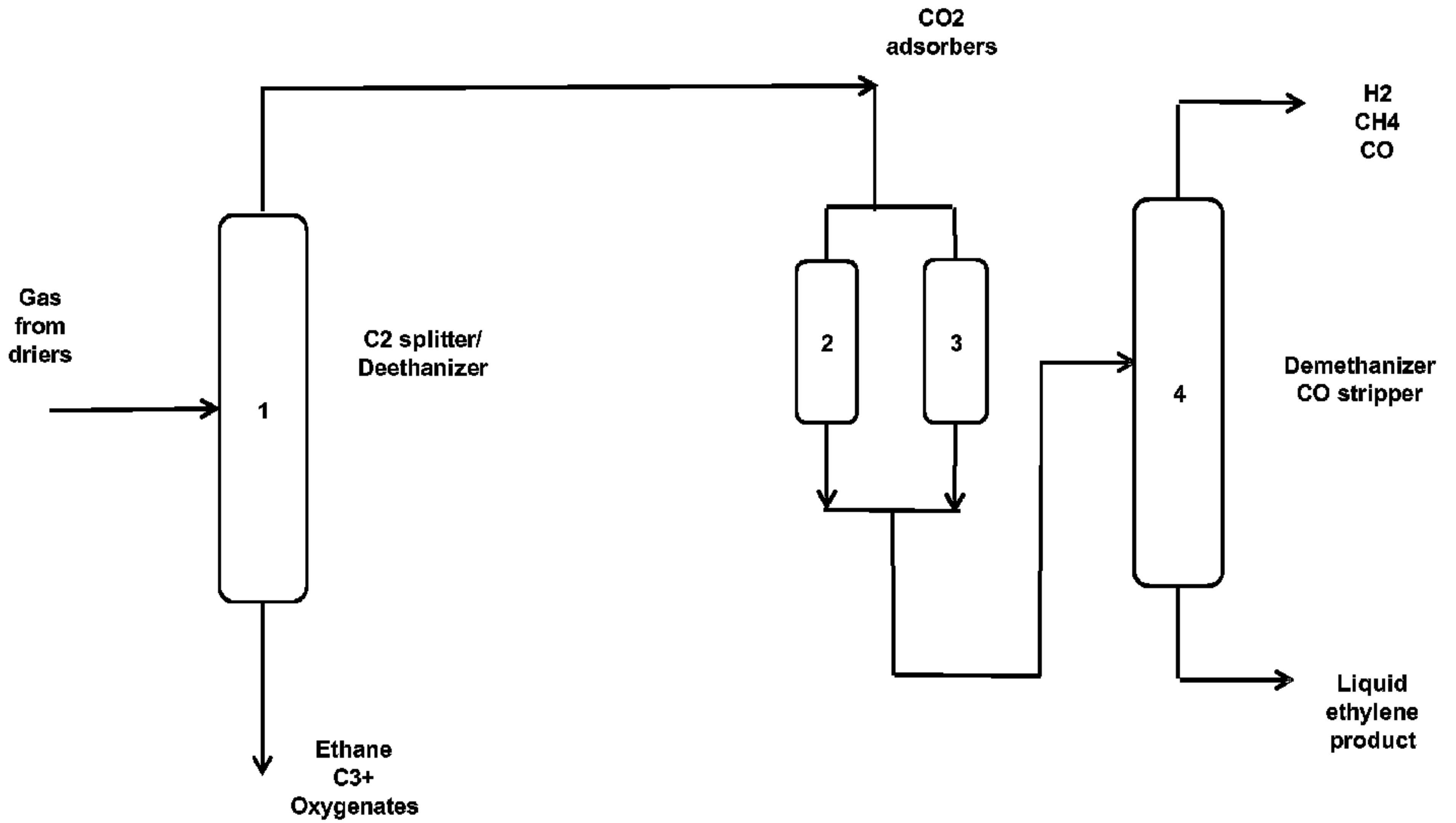


Fig 1