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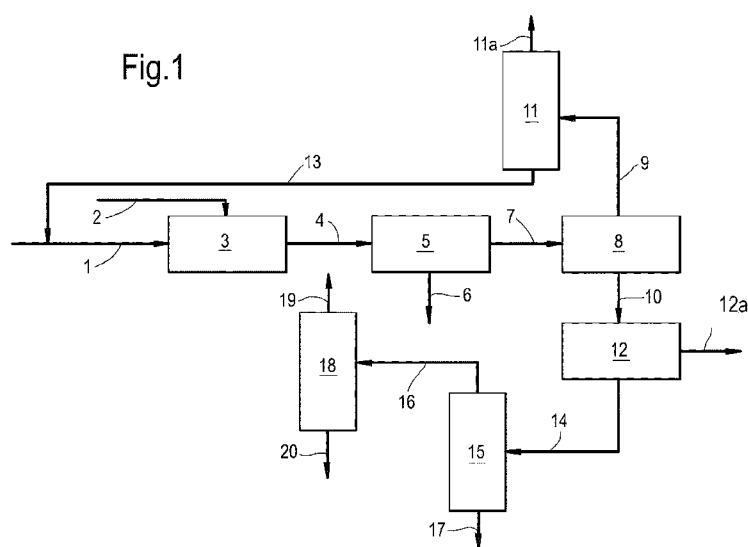
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(54) **Title:** PROCESS FOR THE OXIDATIVE COUPLING OF METHANE



(57) **Abstract:** The invention relates to a process for the oxidative coupling of methane to one or more C<sub>2</sub>+ hydrocarbons, comprising a reaction step which comprises subjecting a gas stream comprising methane and air to methane oxidative coupling conditions resulting in a gas stream comprising nitrogen, methane and ethylene; a sorption step which comprises contacting the gas stream comprising nitrogen, methane and ethylene resulting from the reaction step with a sorption agent which has an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene, resulting in sorption of ethylene and optionally methane by the sorption agent and in a gas stream comprising nitrogen and optionally methane; and a desorption step which comprises desorbing sorbed ethylene and optionally methane resulting in a gas stream comprising ethylene and optionally methane.



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## PROCESS FOR THE OXIDATIVE COUPLING OF METHANE

Field of the invention

The present invention relates to a process for the  
5 oxidative coupling of methane.

Background of the invention

Methane is a valuable resource which is used not only as  
a fuel, but is also used in the synthesis of chemical  
compounds such as higher hydrocarbons.

10 The conversion of methane to other chemical compounds can  
take place via indirect conversion wherein methane is  
reformed to synthesis gas (hydrogen and carbon monoxide),  
followed by reaction of the synthesis gas in a Fischer-  
Tropsch process. However, such indirect conversion is costly  
15 and consumes a lot of energy.

Consequently, it is desirable for industry to be able to  
convert methane directly to other chemical compounds without  
requiring the formation of intermediates such as synthesis  
gas. To this end, there has been increasing focus in recent  
20 years on the development of processes for the oxidative  
coupling of methane (OCM).

The oxidative coupling of methane converts methane into  
saturated and unsaturated, non-aromatic hydrocarbons having 2  
or more carbon atoms, including ethylene. In this process, a  
25 gas stream comprising methane is contacted with an OCM  
catalyst and with an oxidant, such as oxygen or air. In such  
a process, the oxygen is adsorbed on the catalyst's surface.  
Methane molecules are then converted into methyl radicals.  
Two methyl radicals are first coupled into one ethane  
30 molecule, which is then dehydrogenated into ethylene via an  
ethyl radical intermediate. Said ethane and ethylene may  
further react into saturated and unsaturated C3+

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hydrocarbons, including propane, propylene, butane, butene, etc. Usually, the gas stream leaving an OCM process contains a mixture of water, optionally hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane,  
5 propylene, butane, butene and saturated and unsaturated hydrocarbons having 5 or more carbon atoms.

In general, the conversion that can be achieved in an OCM process is relatively low. Besides, at a higher conversion, the selectivity decreases so that it is generally desired to  
10 keep the conversion low. As a result, a relatively large amount of unconverted methane leaves the OCM reactor. The proportion of unconverted methane in the OCM product gas stream may be as high as 60 to 80 mole% based on the total molar amount of the gas stream. This unconverted methane has  
15 to be recovered from the desired products, such as ethylene and other saturated and unsaturated hydrocarbons having 2 or more carbon atoms, which are also present in such gas streams.

It is known to separate the gas stream leaving an OCM  
20 process in the following way. Acid gas (mainly CO<sub>2</sub>) is removed in two stages, the first stage is an aqueous amine absorption system, using for example monoethanolamine (MEA), and the second stage removes final traces of CO<sub>2</sub> by scrubbing against aqueous NaOH. The CO<sub>2</sub>-free gas is dried in a  
25 dessicant bed and processed in a separation train similar to that used in conventional ethylene plants. The separation sequence comprises a front end demethanizer, deethanizer, C2 splitter, depropanizer, C3 splitter, and a debutanizer. The cryogenic needs for separation are met by a propylene-  
30 ethylene cascade refrigeration system that requires ethylene refrigerant only for the demethanization stage.

Thus, it is known to separate methane from saturated and unsaturated hydrocarbons having 2 or more carbon atoms, such

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as ethylene, by means of cryogenic distillation in so-called "demethanizer" columns. In cryogenic distillation, a relatively high pressure (in general: 23 to 35 bar) and a relatively low (cryogenic) temperature (in general: -120 to -70 °C) are applied to effect the separation of methane. The use of cryogenic distillation following an OCM process is for example disclosed in US5113032 and US5025108.

US4754093, US4751336 and US4814539 describe processes for the oxidative coupling of lower alkanes wherein the produced ethylene is adsorbed to be separated from methane and nitrogen and a further desorption step to recover the produced ethylene. US 2015/065767 describes a process for converting alkanes such as methane into C<sub>2</sub>+ olefins using a substantially non-cryogenic separation of the C<sub>2</sub> components from the hydrocarbons (e.g., methane) present in the reaction mixture.

An object of the invention is to provide a technically advantageous, efficient and affordable process for the oxidative coupling of methane, using air as the oxidant, including a step wherein a product gas stream comprising (unconverted) methane and ethylene (product) is separated into a gas stream comprising the methane and another gas stream comprising the ethylene, more especially in a case where such gas stream to be separated comprises a relatively high proportion of unconverted methane. Such technically advantageous process would preferably result in a lower energy demand and/or lower capital expenditure.

#### Summary of the invention

Surprisingly it was found that such technically advantageous process, resulting in a lower energy demand and/or lower capital expenditure, may be provided by subjecting a gas stream comprising nitrogen, methane and ethylene, resulting from subjecting methane and air to

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methane oxidative coupling conditions, to the following two steps: (1) a sorption step which comprises contacting the gas stream comprising nitrogen, methane and ethylene with a sorption agent which has an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene, resulting in sorption of ethylene and optionally methane by the sorption agent and in a gas stream comprising nitrogen and optionally methane; and (2) a desorption step which comprises desorbing sorbed ethylene and optionally methane resulting in a gas stream comprising ethylene and optionally methane

Accordingly, the present invention relates to a process for the oxidative coupling of methane to one or more C2+ hydrocarbons, comprising

a reaction step which comprises subjecting a gas stream comprising methane and air to methane oxidative coupling conditions resulting in a gas stream comprising nitrogen, methane and ethylene;

a sorption step which comprises contacting the gas stream comprising nitrogen, methane and ethylene resulting from the reaction step with a sorption agent which has an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene, resulting in sorption of ethylene and optionally methane by the sorption agent and in a gas stream comprising nitrogen and optionally methane; and

a desorption step which comprises desorbing sorbed ethylene and optionally methane resulting in a gas stream comprising ethylene and optionally methane.

#### Brief description of the drawings

Figure 1 shows an embodiment of the present invention, in which the gas stream that is subjected to the sorption step additionally comprises components other than nitrogen,

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methane and ethylene, namely optionally hydrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons.

Detailed description of the invention

Within the present specification, by "methane oxidative  
5 coupling catalyst" reference is made to a catalyst for the oxidative coupling of methane. Both terms may be used interchangeably. Analogously, by "methane oxidative coupling conditions" reference is made to conditions for the oxidative coupling of methane, which terms may also be used  
10 interchangeably.

Within the present specification, "C2+ hydrocarbons" are hydrocarbons having 2 or more carbon atoms. Likewise, within the present specification, "C3+ hydrocarbons" are hydrocarbons having 3 or more carbon atoms.

15 Within the present specification, by "substantially no" in relation to the amount of a specific component in a gas stream, it is meant an amount which is at most 1,000, preferably at most 500, preferably at most 100, preferably at most 50, more preferably at most 30, more preferably at most  
20 20, and most preferably at most 10 ppmw of the component in question, based on the amount (i.e. weight) of said gas stream.

Within the present specification, where reference is made to relative (e.g. molar) amounts of components in a gas  
25 stream, such relative amounts are to be selected such that the total amount of said gas stream does not exceed 100%.

While the process of the present invention and the streams used in said process are described in terms of "comprising", "containing" or "including" one or more various  
30 described steps and components, respectively, they can also "consist essentially of" or "consist of" said one or more various described steps and components, respectively."

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In the reaction step of the process of the present invention, a gas stream comprising methane and air is subjected to methane oxidative coupling conditions resulting in a gas stream comprising nitrogen, methane and ethylene.

5 In the above-mentioned reaction step, one gas stream comprising methane and air may be fed to a reactor. Alternatively, two or more gas streams may be fed to the reactor, which gas streams form a combined gas stream comprising methane and air inside the reactor. For example,  
10 one gas stream comprising air and another gas stream comprising methane may be fed to the reactor separately.

The reactor may be any reactor suitable for the oxidative coupling of methane, such as a fixed bed reactor with axial or radial flow and with inter-stage cooling or a fluidized  
15 bed reactor equipped with internal and external heat exchangers.

Preferably, subjecting the gas stream comprising methane and air to methane oxidative coupling conditions comprises contacting said gas stream with a methane oxidative coupling  
20 catalyst, as further described below.

In one embodiment of the present invention, a catalyst composition comprising a methane oxidative coupling catalyst may be packed along with an inert packing material, such as quartz, into a fixed bed reactor having an appropriate inner  
25 diameter and length.

Optionally, such catalyst composition may be pretreated at high temperature to remove moisture and impurities therefrom. Said pretreatment may take place, for example, at a temperature in the range of from 100-300 °C for about one  
30 hour in the presence of an inert gas such as helium.

Various processes and reactor set-ups are described in the OCM field and the process of the present invention is not limited in that regard. The person skilled in the art may

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conveniently employ any of such processes in the reaction step of the process of the present invention.

Suitable processes include those described in EP0206042A1, US4443649, CA2016675, US6596912, US20130023709,  
5 WO2008134484 and WO2013106771.

As used herein, the term "reactor feed" is understood to refer to the totality of the gas stream(s) at the inlet(s) of the reactor. Thus, as will be appreciated by one skilled in the art, the reactor feed is often comprised of a combination  
10 of one or more gas stream(s), such as a methane stream, an air stream, a recycle gas stream, etc.

During the oxidative coupling of methane, a reactor feed comprising methane and air is introduced into the reactor, so that a gas stream comprising methane and air is contacted  
15 with a methane oxidative coupling catalyst inside that reactor. Optionally, the reactor feed may further comprise minor components of the methane feed (ethane, propane etc.) or the methane recycle stream (e.g. ethane, ethylene, propane, propylene, CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O).

Advantageously, in the present invention wherein air is used as the oxidant, there is no need to separately add an inert gas, such as nitrogen, argon or helium, as diluent to the above-mentioned reactor feed comprising methane and oxygen. For the nitrogen from the air as fed to the reaction  
25 step already acts as such diluent. The nitrogen from the air ensures that heat generated during the exothermic reaction is more easily dissipated across the entire reactor volume, which in turn simplifies the reactor cooling design. That is, a milder temperature profile is developed which minimizes the  
30 number of heat exchangers (for example coolers) required to remove the heat from the reactor.

Further, advantageously, by using air as the oxidant instead of a high purity oxygen gas stream (e.g. at least 95

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mole% of oxygen), there is no need to first separate high purity oxygen from air in an expensive air separation unit upstream of the OCM reactor. As will be described hereinbelow, the nitrogen coming from the air is separated in  
5 a post-reaction separation procedure which has to be carried out any way in order to remove other components such as above-mentioned hydrogen (H<sub>2</sub>) and carbon monoxide (CO).

In the reaction step of the process of the present invention, methane and air may be added to the reactor as  
10 mixed feed, optionally comprising further components therein, at the same reactor inlet. Alternatively, the methane and air may be added in separate feeds, optionally comprising further components therein, to the reactor at the same reactor inlet or at separate reactor inlets.

15 In the reaction step of the process of the present invention, the methane:oxygen molar ratio in the reactor feed may be in the range of from 2:1 to 10:1, more preferably 3:1 to 6:1. Such methane:oxygen molar ratios correspond to methane:air molar ratios of 2:4.8 to 10:4.8 and 3:4.8 to  
20 6:4.8, respectively.

Methane may be present in the reactor feed in a concentration of at least 35 mole%, more preferably at least 40 mole%, relative to the reactor feed. Further, methane may be present in the reactor feed in a concentration of at most  
25 90 mole%, more preferably at most 85 mole%, most preferably at most 80 mole%, relative to the reactor feed. Thus, in the present invention, methane may for example be present in the reactor feed in a concentration in the range of from 35 to 90 mole%, more preferably 40 to 85 mole%, most preferably 40 to  
30 80 mole%, relative to the reactor feed.

In general, the oxygen concentration in the reactor feed should be less than the concentration of oxygen that would

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form a flammable mixture at either the reactor inlet or the reactor outlet at the prevailing operating conditions.

Air may be present in the reactor feed in a concentration of at least 10 mole%, more preferably at least 15 mole%, most preferably at least 20 mole%, relative to the reactor feed. Further, air may be present in the reactor feed in a concentration of at most 65 mole%, more preferably at most 60 mole%, relative to the reactor feed. Thus, in the present invention, air may for example be present in the reactor feed in a concentration in the range of from 10 to 65 mole%, more preferably 15 to 60 mole%, most preferably 20 to 60 mole%, relative to the reactor feed.

The oxygen concentration in the reactor feed is determined by the above-mentioned relative amount of air, which comprises 21 mole% of oxygen, that is present in the reactor feed. Thus, oxygen may be present in the reactor feed in a concentration of at least 2.1 mole%, more preferably at least 3.2 mole%, most preferably at least 4.2 mole%, relative to the reactor feed. Further, oxygen may be present in the reactor feed in a concentration of at most 13.7 mole%, more preferably at most 12.6 mole%, relative to the reactor feed. Thus, in the present invention, oxygen may for example be present in the reactor feed in a concentration in the range of from 2.1 to 13.7 mole%, more preferably 3.2 to 12.6 mole%, most preferably 4.2 to 12.6 mole%, relative to the reactor feed.

In the above-mentioned reaction step, a reactor feed comprising methane and air is subjected to methane oxidative coupling conditions, which as discussed above, may comprise contacting said gas stream with a methane oxidative coupling catalyst so that methane is converted to one or more C<sub>2</sub>+ hydrocarbons. Suitably, the reactor temperature in said reaction step is in the range of from 500 to 1000 °C.

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Preferably, said conversion is effected at a reactor temperature in the range of from 700 to 1000 °C, more preferably in the range of from 750 to 900 °C.

In a preferred embodiment, said conversion of methane to one or more C<sub>2</sub>+ hydrocarbons is effected at a reactor pressure in the range of from 2 to 20 bar, more preferably 5 to 15 bar.

According to the present invention, the above-mentioned methane oxidative coupling catalyst may be any methane oxidative coupling catalyst. Generally, the catalyst may contain one or more of manganese, one or more alkali metals (e.g. sodium) and tungsten. Preferably, the catalyst contains manganese, one or more alkali metals (e.g. sodium) and tungsten. Said carrier may be unsupported or supported. In particular, the catalyst may be a mixed metal oxide catalyst containing manganese, one or more alkali metals (e.g. sodium) and tungsten. Further, the catalyst may be a supported catalyst, such as a catalyst comprising manganese, one or more alkali metals (e.g. sodium) and tungsten on a carrier. The carrier may be any carrier, such as silica or a metal-containing carrier. A particular suitable catalyst comprises manganese, tungsten and sodium on a silica carrier (Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>).

Suitable methane oxidative coupling catalysts are described in the following publications.

Chua et al. studied the oxidative coupling of methane for the production of ethylene over sodium-tungsten-manganese-supported silica catalyst (Na-W-Mn/SiO<sub>2</sub>) in Applied Catalysis A: General 343 (2008) 142-148.

The performance of Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst was further reviewed by Arndt et al. in Applied Catalysis A: General 425-426 (2012) 53-61 and Lee et al. in Fuel 106 (2013) 851-857.

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US20130023709 describes the high throughput screening of catalyst libraries for the oxidative coupling of methane and tests various catalysts including catalysts comprising sodium, manganese and tungsten on silica and zirconia  
5 carriers.

US20140080699 describes a specific method for the preparation of catalysts such as  $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst which is said to provide an improved catalyst material.

Various manganese and titanium-containing catalysts for  
10 the oxidative coupling of methane are researched in the literature and are disclosed in various patent publications including Gong et al. Catalysis Today 24 (1995), 259-261, Gong et al. Catalysis Today 24 (1995), 263-264, Jeon et al. Applied Catalysis A: General 464-465 (2013) 68-77, US4769508  
15 and US20130178680.

In general, the gas stream comprising nitrogen, methane and ethylene resulting from the above-described reaction step also comprises water. Water may easily be removed from said gas stream, for example by cooling down the gas stream from  
20 the reaction temperature to a lower temperature, for example room temperature, so that the water condenses and can then be removed from the gas stream. Therefore, preferably, in an embodiment wherein the gas stream resulting from the above-described reaction step comprises nitrogen, methane, ethylene  
25 and water, water is removed from such gas stream in the above-mentioned way, preferably before the below-described sorption step is carried out.

Such condensing step, as described above, may be followed by a drying step in order to remove substantially all water,  
30 also preferably before the below-described sorption step is carried out. For example, such drying may be carried out by contacting the gas stream with an absorption agent which has a high affinity for water, such as for example triethylene

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glycol (TEG), for example at a temperature in the range of from 30 to 50 °C, suitably about 40 °C. Alternatively, such drying may be carried out by contacting the gas stream with molecular sieves (or "mol sieves"), suitably at a relatively low temperature in the range of from 10 to 25 °C. Using molecular sieves is preferred in a case where the remaining water content should be as low as possible.

The removal of water before the below-described sorption step, as described above, is preferred because then advantageously less sorption agent may be used in the latter step since there is less or substantially no water to be sorbed by the sorption agent. Further, by removing water at this stage, advantageously less or substantially no water will interfere with downstream purification of gas streams coming from the below-described sorption step and/or desorption step.

Further, in the process of the present invention, the gas stream comprising nitrogen, methane and ethylene resulting from the above-described reaction step is subjected to a sorption step. Suitably, the gas stream that is subjected to the sorption step comprises 25 to 56 mole% of nitrogen, more suitably 30 to 50 mole% of nitrogen; 20 to 70 mole% of methane, more suitably 25 to 65 mole% of methane; 0.1 to 15 mole% of ethylene, more suitably 0.5 to 15 mole % of ethylene, even more suitably 0.5 to 8 mole% of ethylene; and 0 to 10 mole% of oxygen, more suitably 0 to 5 mole% of oxygen. Said relative amounts are based on the total amount of the gas stream.

In the sorption step of the process of the present invention, the gas stream comprising nitrogen, methane and ethylene resulting from the reaction step is contacted with a sorption agent which has an affinity for nitrogen which is lower than that for methane which in turn is lower than that

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for ethylene, resulting in sorption of ethylene and optionally methane by the sorption agent and in a gas stream comprising nitrogen and optionally methane. That is to say, the gas stream resulting from the sorption step comprises  
5 nitrogen and optionally methane that is not sorbed by the sorption agent. In particular, the amount of methane in the gas stream resulting from the sorption step is 0 to 100%, based on the amount of methane in the gas stream that is subjected to the sorption step. The latter percentage may  
10 also be referred to as "methane rejection" (methane not being sorbed, but "rejected"). Such "methane rejection" may be varied by varying the pressure, temperature, nature of the sorption agent, and/or configuration of the sorption-desorption system.

15 Thus, in one embodiment, the sorption step results in sorption of ethylene by the sorption agent and in a gas stream comprising nitrogen and methane; and the desorption step comprises desorbing sorbed ethylene resulting in a gas stream comprising ethylene.

20 In another embodiment, the sorption step results in sorption of ethylene and methane by the sorption agent and in a gas stream comprising nitrogen; and the desorption step comprises desorbing sorbed ethylene and methane resulting in a gas stream comprising ethylene and methane.

25 The amount of (rejected) methane in the gas stream resulting from the sorption step may be at most 100%, or at most 99%, or at most 98%, or at most 95%, or at most 90%, based on the amount of methane in the gas stream that is subjected to the sorption step. Further, the amount of  
30 (rejected) methane in the gas stream resulting from the sorption step may be at least 10%, or at least 20%, or at least 30%, or at least 40%, or at least 50%, or at least 60%, based on the amount of methane in the gas stream that is

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subjected to the sorption step. Thus, in those embodiments wherein a certain amount of methane is rejected in the sorption step, the amount of (rejected) methane in the gas stream resulting from the sorption step may for example be 20  
5 to 100%, or 30 to 100%, or 40 to 100%, or 50 to 100%, or 60 to 100%, based on the amount of methane in the gas stream that is subjected to the sorption step.

In the sorption step of the process of the present invention, a sorption agent is used. In the present  
10 specification, "sorption" means a process in which one substance (the sorption agent) takes up or holds or retains another substance by absorption, adsorption or a combination of both.

Further, said sorption agent used in the sorption step of  
15 the process of the present invention has an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene. This means that under the conditions applied in said sorption step, including pressure and temperature which are further defined hereinbelow, said  
20 sorption agent has an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene. This implies that in the process of the present invention such sorption agent should be used in the sorption step, that the molar ratio of sorbed ethylene to sorbed  
25 methane is greater than 1:1, assuming equal partial pressures for ethylene and methane. Preferably, said ratio is equal to or higher than 1.1:1, more preferably equal to or higher than 5:1. Said ratio may be up to 50:1, or may be up to 40:1, or may be up to 30:1, or may be up to 20:1, or may be up to  
30 10:1. For example, said ratio is in the range of from 1.1:1 to 50:1, or from 1.1:1 to 20:1, from 5:1 to 10:1, or from 5:1 to 20:1. Sorption agents suitable to be used in the present invention may be selected by comparing the extent of sorption

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of methane with the extent of sorption of ethylene, under any given temperature and pressure conditions for a variety of known sorption agents, assuming equal partial pressures for ethylene and methane. Therefore, a wide range of sorption agents may be used since the only criterion in the present invention is that the sorption agent should have an affinity for nitrogen which is lower than that for methane which in turn is lower than that for ethylene. Without any limitation, examples of suitable sorption agents are activated carbons; 5 molecular sieves and zeolites (e.g. zeolite 13X, zeolite 5A, ZSM-5, SAPO-34); mesoporous silicas (e.g. SBA-2, SBA-15); porous silicas (e.g. CMK-3, silicate-1); clay heterostructures; Engelhard Titanosilicates (ETS; e.g. ETS-4, ETS-10); porous coordination polymers (PCPs); metal-organic 10 frameworks (MOFs); Carbon Organic Frameworks (COFs); Porous Aromatic Frameworks (PAFs); and Zeolitic Imidazolate Framework (ZIFs). Suitable sorption agents are for example disclosed in US20150065767 and US20140249339.

The pressure in the sorption step of the process of the present invention may vary within wide ranges. Preferably, 20 said pressure is equal to or higher than atmospheric pressure and at most 30 bar, more preferably at most 15 bar. More preferably, said pressure is of from 5 to 30 bar, more preferably 5 to 15 bar, most preferably 7 to 13 bar. In the reaction step of the process of the present invention, air 25 may be fed at a pressure in the range of from 5 to 30 bar, preferably 5 to 15 bar, more preferably 7 to 13 bar. This implies advantageously that the gas stream comprising nitrogen, methane and ethylene resulting from the reaction step generally need not be compressed before subjecting it to 30 the sorption step. Thus, preferably, the pressure at which air is fed in the reaction step is the same as the pressure in the sorption step. Still further, the fact that air may be

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fed in the reaction step at a relatively high pressure makes that the volume of the air is relatively small, which is advantageous in that a smaller OCM reactor may be used, the relative proportion of oxygen in air (78 vol.% of nitrogen and 21 vol.% of oxygen) being relatively small as compared to  
5 for example a high purity oxygen gas stream (e.g. at least 95 mole% of oxygen).

The temperature in the sorption step of the process of the present invention may also vary within wide ranges.  
10 Preferably, said temperature is in the range of from 0 to 100 °C, more preferably 10 to 90 °C, most preferably 25 to 80 °C. Advantageously, in the present invention, said sorption step may be carried out at a non-cryogenic temperature (e.g. of from 0 to 100 °C as mentioned above).

15 In the desorption step of the process of the present invention, ethylene and optionally methane that are sorbed by the sorption agent are desorbed, resulting in a gas stream comprising ethylene and optionally methane. That is to say, the latter gas stream resulting from the desorption step  
20 comprises ethylene and optionally methane that are desorbed from the sorption agent.

Preferably, in the desorption step of the process of the present invention, desorption is effected by reducing the pressure. That is to say, the pressure in the desorption step  
25 is lower than the pressure in the sorption step. This is usually referred to as "Pressure Swing Adsorption" (PSA). In the embodiment wherein desorption in the desorption step is effected by reducing the pressure, the pressure in the sorption step is preferably in the range of from 5 to 30 bar,  
30 more preferably 5 to 15 bar, more preferably 7 to 13 bar.

In a case wherein a relatively low pressure (e.g. at most 15 bar) is used in the sorption step, advantageously no or only part of the methane is sorbed in addition to ethylene.

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Thus, advantageously, in the sorption step of the process of the present invention, a relatively low pressure is applied (e.g. of from 5 to 15 bar as mentioned above). In addition, such low pressure advantageously results in that relatively less compression of the gas stream may be needed. It is especially advantageous that the pressure that may be needed in the sorption step of the process of the present invention may be the same as the pressure in the preceding (OCM) reaction step. In the latter case, there would be no need at all for any compression of said gas stream in order to carry out said sorption step.

Further, in the embodiment wherein desorption in the desorption step is effected by reducing the pressure, the pressure in the desorption step is preferably in the range of from 0.1 to 3 bar, more preferably 0.5 to 2 bar.

The temperature in the desorption step of the process of the present invention may also vary within wide ranges. Preferably, said temperature is in the range of from 0 to 100 °C, more preferably 10 to 90 °C, most preferably 25 to 80 °C. Advantageously, in the present invention, said desorption step may be carried out at a non-cryogenic temperature (e.g. of from 0 to 100 °C as mentioned above).

Advantageously, the sorption and desorption steps of the process of the present invention make it possible to efficiently separate nitrogen and optionally methane from a gas stream comprising nitrogen, methane and ethylene, resulting from the preceding (OCM) reaction step, at a relatively low pressure (e.g. at most 15 bar as mentioned above) and at a non-cryogenic temperature (e.g. of from 0 to 100 °C as mentioned above).

Preferably, the gas stream comprising nitrogen, methane and ethylene that is subjected to the sorption step of the process of the present invention comprises substantially no

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water. As described above, preferably, any water is removed from said gas stream before the sorption step is carried out. It is also preferred that said gas stream comprising nitrogen, methane and ethylene comprises substantially no hydrogen sulfide.

In the embodiment(s), wherein the sorption step of the present process results in sorption of ethylene by the sorption agent and in a gas stream comprising nitrogen and methane, and the desorption step comprises desorbing sorbed ethylene resulting in a gas stream comprising ethylene, preferably, the present process additionally comprises a distillation step which comprises distilling the gas stream comprising nitrogen and methane resulting from the sorption step, resulting in a top stream comprising nitrogen and a bottom stream comprising methane; and optionally a recycle step which comprises recycling the bottom stream comprising methane resulting from the distillation step to the reaction step.

In the embodiment(s), wherein the sorption step of the present process results in sorption of ethylene and methane by the sorption agent and in a gas stream comprising nitrogen, and the desorption step comprises desorbing sorbed ethylene and methane resulting in a gas stream comprising ethylene and methane, the present process additionally comprises a distillation step which comprises distilling the gas stream comprising ethylene and methane resulting from the desorption step, resulting in a top stream comprising methane and a bottom stream comprising ethylene; and optionally a recycle step which comprises recycling the top stream comprising methane resulting from the distillation step to the reaction step

As is demonstrated in the present Examples, it has surprisingly appeared that advantageously the energy demand,

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especially the demand for compression and refrigeration energy, is significantly lower as compared to a process wherein a sorption and desorption method is not applied after the OCM reaction step, irrespective of whether in the OCM  
5 reaction step of such comparative case only oxygen (no nitrogen) or air is used. Thus, the present process is a process that enables the oxidative coupling of methane and subsequent separation of the product stream comprising nitrogen, methane and ethylene, to recover unconverted  
10 methane and ethylene, in a way that is technically feasible, efficient and affordable since the energy demand is surprisingly lower as compared to the comparative process.

Further, in an embodiment of the process of the present invention, the gas stream comprising nitrogen, methane and  
15 ethylene that is subjected to the sorption step of the process of the present invention additionally comprises components other than said nitrogen, methane and ethylene, such as carbon monoxide, optionally hydrogen, carbon dioxide, ethane and C3+ hydrocarbons. Therefore, in the present  
20 invention, the reaction step may result in a gas stream comprising methane, ethylene, optionally hydrogen, nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons

Suitably, said C3+ hydrocarbons comprise saturated and unsaturated C3+ hydrocarbons, including propane, propylene,  
25 butane and butene, and optionally saturated and unsaturated hydrocarbons having 5 or more carbon atoms.

In the above-mentioned embodiment of the process of the present invention, wherein the reaction step results in a gas stream comprising methane, ethylene, optionally hydrogen,  
30 nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons,

the sorption step comprises contacting the gas stream comprising methane, ethylene, optionally hydrogen, nitrogen,

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carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons resulting from the reaction step with a sorption agent which has an affinity for hydrogen, nitrogen and carbon monoxide which is lower than that for methane which in turn is lower than that for carbon dioxide, ethane, ethylene and C3+ hydrocarbons, resulting in sorption of carbon dioxide, ethane, ethylene, C3+ hydrocarbons and optionally methane by the sorption agent and in a gas stream comprising optionally hydrogen, nitrogen, carbon monoxide and optionally methane;

10 and

the desorption step comprises desorbing sorbed carbon dioxide, ethane, ethylene, C3+ hydrocarbons and optionally methane resulting in a gas stream comprising carbon dioxide, ethane, ethylene, C3+ hydrocarbons and optionally methane.

15 The sorption agents, pressures, temperatures, sorption-desorption method (e.g. PSA) and configuration of the sorption-desorption system as discussed above also apply to the above-mentioned embodiment of the process of the present invention, wherein the gas stream that is subjected to the sorption step (gas stream resulting from the reaction step) comprises methane, ethylene, optionally hydrogen, nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons.

The sorption step in the above-mentioned embodiment of the process of the present invention may result in sorption of ethylene, carbon dioxide, ethane and C3+ hydrocarbons by the sorption agent and in a gas stream comprising optionally hydrogen, nitrogen, carbon monoxide and methane, in which case the desorption step comprises desorbing sorbed ethylene, carbon dioxide, ethane and C3+ hydrocarbons resulting in a gas stream comprising ethylene, carbon dioxide, ethane and C3+ hydrocarbons. Preferably, in such case, the process of the present invention additionally comprises a distillation step which comprises distilling the gas stream comprising

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optionally hydrogen, nitrogen, carbon monoxide and methane resulting from the sorption step, resulting in a top stream comprising optionally hydrogen, nitrogen and carbon monoxide and a bottom stream comprising methane. Optionally, said  
5 bottom stream comprising methane is recycled to the reaction step.

Further, the sorption step in the above-mentioned embodiment of the process of the present invention may result in sorption of ethylene, methane, carbon dioxide, ethane and  
10 C3+ hydrocarbons by the sorption agent and in a gas stream comprising optionally hydrogen, nitrogen and carbon monoxide, in which case the desorption step comprises desorbing sorbed ethylene, methane, carbon dioxide, ethane and C3+ hydrocarbons resulting in a gas stream comprising ethylene,  
15 methane, carbon dioxide, ethane and C3+ hydrocarbons.

Further, preferably, in the above-mentioned embodiments, the process of the present invention additionally comprises a carbon dioxide removal step which comprises removing carbon dioxide from the gas stream comprising carbon dioxide,  
20 ethylene, ethane, C3+ hydrocarbons and optionally methane resulting from the desorption step, resulting in a gas stream comprising ethylene, ethane, C3+ hydrocarbons and optionally methane. In said carbon dioxide removal step, carbon dioxide may be removed by any known method, such as treatment with an  
25 amine and then with a caustic agent, such as an aqueous monoethanolamine (MEA) absorption system and aqueous NaOH, respectively, as already mentioned above in the introduction of this specification. In a case where said carbon dioxide removal step involves the use of water, said step normally  
30 also involves the removal of that water, suitably followed by a drying step. Such drying step may be carried out in order to remove substantially all water and may be carried out in

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one of the ways as exemplified above in relation to the optional drying step after a condensing step.

Alternatively, said carbon dioxide removal step may be carried out before the sorption step and before any water removal step(s). This is advantageous, first of all in that the gas stream to be subjected to the carbon dioxide removal step may not need to be compressed in a case where the latter gas stream still has a sufficiently high pressure, for example of from 5 to 30 bar or 5 to 15 bar. Secondly, the removal of carbon dioxide before the sorption step is advantageous in that then less sorption agent may be used in the latter step since there is substantially no carbon dioxide to be sorbed by the sorption agent. This alternative embodiment, wherein the carbon dioxide removal step is carried out before the sorption step and before any water removal step(s), may also be applied to cases wherein no air is used as the oxidant, but for example a high purity oxygen gas stream (not according to the invention). In a case where in the present invention, said carbon dioxide removal step is carried out before the sorption step, said carbon dioxide removal step comprises removing carbon dioxide from the gas stream comprising methane, ethylene, optionally hydrogen, nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons resulting from the reaction step, resulting in a gas stream comprising methane, ethylene, optionally hydrogen, nitrogen, carbon monoxide, ethane and C3+ hydrocarbons.

The above-described embodiments of the process of the present invention, comprising the sorption step and desorption step followed or preceded by the carbon dioxide removal step, may additionally comprise a (first) distillation step wherein either (i) the gas stream resulting from the carbon dioxide removal step as carried out after the desorption step or (ii) the gas stream resulting from the

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desorption step as carried out after the carbon dioxide removal step and sorption step, respectively, is distilled. Said distillation step will be further described below with reference to said case (i) only.

5        Preferably, in a case where said gas stream, resulting from said carbon dioxide removal step, comprises methane, said first distillation step comprises distilling the gas stream comprising ethylene, ethane, C3+ hydrocarbons and methane resulting from the carbon dioxide removal step,  
10        resulting in a top stream comprising methane and a bottom stream comprising ethylene, ethane and C3+ hydrocarbons. Optionally, said top stream comprising methane is recycled to the reaction step. Further, the process of the present invention may additionally comprise a distillation step which  
15        comprises distilling the above-mentioned bottom stream comprising ethylene, ethane and C3+ hydrocarbons, preferably resulting in a top stream comprising ethylene and ethane and a bottom stream comprising C3+ hydrocarbons or alternatively resulting in a top stream comprising ethylene and a bottom  
20        stream comprising ethane and C3+ hydrocarbons. Further, preferably, the process of the present invention additionally comprises a distillation step which comprises distilling the above-mentioned top stream comprising ethylene and ethane, resulting in a top stream comprising ethylene and a bottom  
25        stream comprising ethane. Further, the process of the present invention may additionally comprise a distillation step which comprises distilling the above-mentioned bottom stream comprising ethane and C3+ hydrocarbons, resulting in a top stream comprising ethane and a bottom stream comprising C3+  
30        hydrocarbons.

Alternatively, in a case where said gas stream, resulting from said carbon dioxide removal step, comprises methane, said first distillation step may comprise distilling the gas

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stream comprising ethylene, ethane, C3+ hydrocarbons and methane resulting from the carbon dioxide removal step, resulting in a top stream comprising methane and ethylene and a bottom stream comprising ethane and C3+ hydrocarbons.

5 Further, the process of the present invention may additionally comprise a distillation step which comprises distilling the above-mentioned top stream comprising methane and ethylene, resulting in a top stream comprising methane and a bottom stream comprising ethylene. Optionally, said top  
10 stream comprising methane is recycled to the reaction step. Further, the process of the present invention may additionally comprise a distillation step which comprises distilling the above-mentioned bottom stream comprising ethane and C3+ hydrocarbons, resulting in a top stream  
15 comprising ethane and a bottom stream comprising C3+ hydrocarbons.

In another case where said gas stream, resulting from said carbon dioxide removal step, does not comprise methane, said first distillation step may comprise distilling the gas  
20 stream comprising ethylene, ethane and C3+ hydrocarbons resulting from the carbon dioxide removal step, preferably resulting in a top stream comprising ethylene and ethane and a bottom stream comprising C3+ hydrocarbons or alternatively resulting in a top stream comprising ethylene and a bottom  
25 stream comprising ethane and C3+ hydrocarbons. Further, preferably, the process of the present invention additionally comprises a distillation step which comprises distilling the above-mentioned top stream comprising ethylene and ethane, resulting in a top stream comprising ethylene and a bottom  
30 stream comprising ethane. Further, the process of the present invention may additionally comprise a distillation step which comprises distilling the above-mentioned bottom stream comprising ethane and C3+ hydrocarbons, resulting in a top

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stream comprising ethane and a bottom stream comprising C3+ hydrocarbons.

An example of said embodiment of the process of the present invention, wherein the gas stream that is subjected to the sorption step additionally comprises components other than nitrogen, methane and ethylene, namely optionally hydrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons, is schematically shown in Figure 1.

Hereinafter, the combination of ethylene, ethane and C3+ hydrocarbons may also be referred to as C2+ hydrocarbons.

In said Figure 1, a gas stream 1 comprising methane and an air stream 2 are fed to a methane oxidative coupling (OCM) reactor 3 containing an OCM catalyst and operating under OCM conditions. Product stream 4 originating from OCM reactor 3 comprises water, methane, ethylene, hydrogen, nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons. Said stream 4 is fed to condensation vessel 5 where water is removed via stream 6. Gas stream 7 comprising methane, ethylene, hydrogen, nitrogen, carbon monoxide, carbon dioxide, ethane and C3+ hydrocarbons originating from condensation vessel 5 is fed to sorption and desorption unit 8. Optionally, before gas stream 7 is fed to sorption and desorption unit 8, it is sent to a drying unit (not shown in Figure 1) in order to remove substantially all water.

Sorption and desorption unit 8 comprises a sorption agent which has an affinity for hydrogen, nitrogen and carbon monoxide which is lower than that for methane which in turn is lower than that for carbon dioxide, ethane, ethylene and C3+ hydrocarbons. The pressure of gas stream 7 may be of from 5 to 15 bar. Carbon dioxide, ethane, ethylene and C3+ hydrocarbons are sorbed by the sorption agent. Further, a gas stream 9 comprising nitrogen, hydrogen, carbon monoxide and methane leaves sorption and desorption unit 8, which

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nitrogen, hydrogen, carbon monoxide and methane are not sorbed by the sorption agent in sorption and desorption unit 8. Gas stream 9 is sent to distillation column 11.

In distillation column 11, gas stream 9 comprising  
5 nitrogen, hydrogen, carbon monoxide and methane is distilled such that separation between on the one hand nitrogen, hydrogen and carbon monoxide and on the other hand methane is effected. That is, a top stream 11a comprising nitrogen, hydrogen and carbon monoxide and a bottom stream 13  
10 comprising methane leave distillation column 11. Said bottom stream 13 is advantageously recycled to OCM reactor 3, for further conversion of the recovered methane.

After some time, the feed of gas stream 7 to sorption and desorption unit 8 is stopped and the pressure in said unit is  
15 reduced. For example, the pressure in sorption and desorption unit 8 may be reduced to a pressure in the range of from 0.1 to 3 bar in a case wherein during the sorption step the pressure is in the range of from 5 to 15 bar, as exemplified above. Through such pressure reduction carbon dioxide and C2+  
20 hydrocarbons that are sorbed by the sorption agent become desorbed. A gas stream 10 comprising carbon dioxide and C2+ hydrocarbons, that are desorbed from the sorption agent, leaves sorption and desorption unit 8 and is sent to carbon dioxide removal unit 12.

25 Once the desorption is completed, the feed of gas stream 7 to sorption and desorption unit 8 is resumed and the above procedure is repeated.

In carbon dioxide removal unit 12, carbon dioxide is removed, via stream 12a, from gas stream 10 comprising carbon  
30 dioxide and C2+ hydrocarbons, in a way as exemplified above, that is to say involving the use of water and the removal of that water. A gas stream 14 comprising C2+ hydrocarbons leaves carbon dioxide removal unit 12. Before gas stream 14

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is sent to distillation column 15, it is sent to a drying unit (not shown in Figure 1) in order to remove substantially all water.

As an alternative, carbon dioxide removal unit 12 may be moved to a position in line 4 directly after OCM reactor 3 in which case condensation vessel 5 may be omitted, since in said carbon dioxide removal unit water is removed at the same time in addition to carbon dioxide. Further, if there is a drying unit in line 7 (optional), as described above, the drying unit in line 14 may be omitted.

In distillation column 15, gas stream 14 comprising C2+ hydrocarbons is distilled such that separation between on the one hand ethylene and ethane and on the other hand C3+ hydrocarbons is effected. That is, a top stream 16 comprising ethylene and ethane and a bottom stream 17 comprising C3+ hydrocarbons leave distillation column 15.

Top stream 16 comprising ethylene and ethane is sent to distillation column 18, wherein it is distilled such that separation between ethylene and ethane is effected. That is, a top stream 19 comprising ethylene and a bottom stream 20 comprising ethane leave distillation column 18.

If in the setup of Figure 1, a gas stream 1 comprising methane of sufficiently high pressure (for example in the range of from 5 to 15 bar, which may be the case for a natural gas stream) is fed to OCM reactor 3, gas compressors would advantageously only be needed in line 2 (compression of air) and in line 10 (compression of gas stream 10 leaving sorption and desorption unit 8, after desorption, and entering carbon dioxide removal unit 12).

The invention is further illustrated by the following Examples.

Examples A-C and Comparative Examples D-E

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In Examples A, B and C exemplifying the present invention and in Comparative Example E, a gas stream comprising methane having a temperature of 40 °C and a pressure of 10 bar (said gas stream originating from a natural gas source) is fed to a methane oxidative coupling (OCM) reactor. In addition, a gas stream comprising air having a temperature of 40 °C and being compressed to 10 bar by a compressor comprising 2 compression stages, is fed to the OCM reactor. Said 2 gas streams form a combined gas stream comprising methane and air inside the OCM reactor, which combined gas stream comprises 46 mole% of methane and 54 mole% of air (methane:air molar ratio = 0.8), that is to say 46 mole% of methane, 11 mole% of oxygen and 43 mole% of nitrogen (methane:oxygen molar ratio = 4). The OCM reactor contains a methane oxidative coupling (OCM) catalyst and is operated under OCM conditions, including a temperature in the range of from 750 to 900 °C and a pressure of 10 bar. The conversion of methane is 35% and the selectivity to ethylene is 100%.

In Examples A, B and C and in Comparative Example E, a product stream comprising 30 mole% of methane, 3 mole% of oxygen, 8 mole% of ethylene, 16 mole% of water and 43 mole% of nitrogen leaves the OCM reactor. Said product stream is cooled to a temperature of 40 °C, thereby condensing out the water which is then separated. Any remaining water in said product stream is removed in a drying unit. After said water removal, said product stream is a gas stream comprising 35.3 mole% of methane, 4.1 mole% of oxygen, 9.5 mole% of ethylene and 51.1 mole% of nitrogen. In Examples A, B and C (not in Comparative Example E), the latter gas stream is fed to a sorption and desorption unit, which comprises a sorption agent which has an affinity for nitrogen (and for oxygen) which is lower than that for methane which in turn is lower than that for ethylene. All of the ethylene is sorbed by the

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sorption agent. In Example A, all of the methane is also sorbed by the sorption agent (methane rejection = 0%). In Example B, 50% of the methane is also sorbed by the sorption agent (methane rejection = 50%). In Example C, no methane is sorbed by the sorption agent (methane rejection = 100%).

In Example A, a gas stream comprising nitrogen and oxygen, and having a temperature of 40 °C and a pressure of 10 bar, leaves the sorption and desorption unit, which nitrogen and oxygen are not sorbed by the sorption agent in the sorption and desorption unit.

In Examples B and C, a gas stream comprising nitrogen, oxygen and methane, and having a temperature of 40 °C and a pressure of 10 bar, leaves the sorption and desorption unit, which nitrogen, oxygen and methane are not sorbed by the sorption agent in the sorption and desorption unit. The latter gas stream is compressed to 17 bar by a compressor comprising 1 compression stage and then cooled to a temperature of -142 °C (Example B) or -138 °C (Example C) in two parallel heat exchangers utilizing the low temperature of the top and/or bottom streams coming from below-described distillation column A. Then said stream is fed to a distillation column having 22 theoretical stages, hereinafter referred to as distillation column A, and distilled, resulting in a top stream comprising nitrogen and oxygen and having a temperature of -159 °C and a pressure of 17 bar and in a bottom stream comprising methane and having a temperature of -112 °C and a pressure of 17 bar. Said top and bottom streams are used to cool the feed streams in order to minimize condenser duty in distillation column A, which is provided by a cascaded methane-ethylene-propane refrigeration cycle.

After some time, in Examples A, B and C, the feed of the gas stream to the sorption and desorption unit is stopped and

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the pressure in said unit is reduced from 10 bar to 1 bar, thereby inducing the desorption step of the process of the present invention. The sorbed components (ethylene and optionally methane) subsequently become desorbed from the sorption agent and leave the sorption and desorption unit at a temperature of 40 °C and a pressure of 1 bar. In all of Examples A, B and C, the latter gas stream is advantageously enriched in ethylene as compared to the gas stream that is fed to the sorption and desorption unit: in Example A, the gas stream leaving the sorption and desorption unit upon desorption comprises all of the ethylene and all of the methane; in Example B, said gas stream comprises all of the ethylene and 50% of the methane; and in Example C, said gas stream comprises all of the ethylene and no methane.

In Examples A and B, the gas stream leaving the sorption and desorption unit upon desorption and comprising ethylene and methane is compressed to 32 bar by a compressor comprising 4 compression stages and then cooled to a temperature of -65 °C (Example A) or -61 °C (Example B) in two parallel heat exchangers utilizing the low temperature of the top stream coming from below-described distillation column B and/or the bottom stream coming from distillation column A. Then said stream is fed to a distillation column having 22 theoretical stages, hereinafter referred to as distillation column B, and distilled, resulting in a top stream comprising methane and having a temperature of -95 °C and a pressure of 31 bar and in a bottom stream comprising ethylene and having a temperature of -12 °C and a pressure of 31 bar. Said top and bottom streams are used to cool the feed streams in order to minimize condenser duty in distillation column B, which is provided by a cascaded ethylene-propane refrigeration cycle.

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In Table 1 below, the reflux ratios and the distillate-to-feed ratios needed to achieve the above separations in distillation columns A and B in Examples A, B and C are mentioned. By said "reflux ratio", reference is made to the molar ratio of the molar flow rate of the "reflux stream", which is that part of the stream that leaves the condenser at the top of the distillation column which is sent back to that column, divided by the molar flow rate of the "distillate", which is that part of the stream that leaves the condenser at the top of the distillation column which is not sent back to that column. By said "distillate-to-feed ratio", reference is made to the molar ratio of the molar flow rate of said "distillate" divided by the molar flow rate of the feed stream that is fed to that column (the "feed").

Table 1

| Example | Distillation column | Reflux ratio | Distillate-to-feed ratio |
|---------|---------------------|--------------|--------------------------|
| A       | B                   | 1.6          | 0.68                     |
| B       | A                   | 1.6          | 0.85                     |
| B       | B                   | 1.9          | 0.52                     |
| C       | A                   | 2.0          | 0.74                     |

In Comparative Example D, a gas stream comprising air of ambient temperature and pressure is fed to an air separation unit (ASU). The ASU is operated such that the following 2 streams leave the ASU: 1) a gas stream comprising nitrogen having a temperature of 40 °C and a pressure of 20 bar (which nitrogen can be subsequently stored); and 2) a gas stream comprising oxygen (purity of 99.5 mole%; 0.5 mole% of nitrogen) having a temperature of 40 °C and a pressure of 10 bar. Said gas stream comprising oxygen is fed to a methane oxidative coupling (OCM) reactor. In addition, a gas stream comprising methane having a temperature of 40 °C and a

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pressure of 10 bar (said gas stream originating from a natural gas source) is fed to a methane oxidative coupling (OCM) reactor. Said 2 gas streams form a combined gas stream comprising methane and oxygen (and a minor amount of  
5 nitrogen) inside the OCM reactor, which combined gas stream comprises 80 mole% of methane and 20 mole% of oxygen (methane:oxygen molar ratio = 4). The OCM reactor contains a methane oxidative coupling (OCM) catalyst and is operated under OCM conditions, including a temperature in the range of  
10 from 750 to 900 °C and a pressure of 10 bar. The conversion of methane is 35% and the selectivity to ethylene is 100%".

In Comparative Example D, a product stream comprising 52 mole% of methane, 6 mole% of oxygen, 14 mole% of ethylene and 28 mole% of water (and a minor amount of nitrogen) leaves the  
15 OCM reactor. Said product stream is cooled to a temperature of 40 °C, thereby condensing out the water which is then separated. Any remaining water in said product stream is removed in a drying unit. After said water removal, said product stream is a gas stream comprising 72.2 mole% of  
20 methane, 8.3 mole% of oxygen, 19.4 mole% of ethylene (and a minor amount of nitrogen). The latter gas stream is compressed to 17 bar by a compressor comprising 1 compression stage and then cooled to a temperature of -99 °C. Then said stream is fed to a distillation column having 22 theoretical  
25 stages, hereinafter referred to as distillation column C, and distilled, resulting in a top stream comprising oxygen (and a minor amount of nitrogen) and having a temperature of -140 °C and a pressure of 17 bar and in a bottom stream comprising methane and ethylene and having a temperature of -104 °C and  
30 a pressure of 17 bar.

In Comparative Example D, said bottom stream comprising methane and ethylene is compressed to 32 bar by a compressor comprising 1 compression stage and the temperature of said

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stream is adjusted to -75 °C in two parallel heat exchangers utilizing the low temperature of the bottom stream coming from distillation column C and the top stream coming from below-described distillation column D. Then said stream is  
5 fed to a distillation column having 22 theoretical stages, hereinafter referred to as distillation column D, and distilled, resulting in a top stream comprising methane and having a temperature of -95 °C and a pressure of 31 bar and in a bottom stream comprising ethylene and having a  
10 temperature of -12 °C and a pressure of 31 bar.

In Table 2 below, the reflux ratios and the distillate-to-feed ratios needed to achieve the above separations in distillation columns C and D in Comparative Example D are mentioned.

15 Table 2

| Comparative Example | Distillation column | Reflux ratio | Distillate-to-feed ratio |
|---------------------|---------------------|--------------|--------------------------|
| D                   | C                   | 20.0         | 0.14                     |
| D                   | D                   | 1.1          | 0.68                     |

In Comparative Example E, the gas stream comprising methane, oxygen, ethylene and nitrogen resulting from the OCM reaction and subsequent water removal, is compressed to 17  
20 bar by a compressor comprising 1 compression stage and then cooled to a temperature of -102 °C. Then said stream is fed to a distillation column having 22 theoretical stages, hereinafter referred to as distillation column E, and distilled, resulting in a top stream comprising nitrogen and  
25 oxygen and having a temperature of -159 °C and a pressure of 17 bar and in a bottom stream comprising methane and ethylene and having a temperature of -104 °C and a pressure of 17 bar. Said top and bottom streams are used to cool the feed streams in order to minimize condenser duty in the distillation

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column, which is provided by a cascaded methane-ethylene-propane refrigeration cycle.

In Comparative Example E, said bottom stream comprising methane and ethylene is compressed to 32 bar by a compressor comprising 1 compression stage and the temperature of said stream is adjusted to -100 °C in two parallel heat exchangers utilizing the low temperature of the bottom stream coming from distillation column E and the top stream coming from below-described distillation column F. Then said stream is fed to a distillation column having 22 theoretical stages, hereinafter referred to as distillation column F, and distilled, resulting in a top stream comprising methane and having a temperature of -95 °C and a pressure of 31 bar and in a bottom stream comprising ethylene and having a temperature of -12 °C and a pressure of 31 bar. Said top and bottom streams are used to cool the feed streams in order to minimize condenser duty in the distillation column, which is provided by a cascaded ethylene-propane refrigeration cycle.

In Table 3 below, the reflux ratios and the distillate-to-feed ratios needed to achieve the above separations in distillation columns E and F in Comparative Example E are mentioned.

Table 3

| Comparative Example | Distillation column | Reflux ratio | Distillate-to-feed ratio |
|---------------------|---------------------|--------------|--------------------------|
| E                   | E                   | 3.6          | 0.66                     |
| E                   | F                   | 0.7          | 0.68                     |

In all of the (Comparative) Examples, methane containing streams separated in the distillation columns may be recycled to the OCM reactor at 10 bar. The temperature reduction by reducing the pressure of such recycle methane containing streams to 10 bar, as well as the temperature reduction by

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reducing the pressure of nitrogen and oxygen containing top (vent) streams to atmospheric pressure, are utilized to cool the feed streams to the distillation columns and in this way the condenser duty provided by refrigeration is reduced.

5 In Table 4 below, the compression and refrigeration energy needed to convert methane into ethylene and to separately recover methane and ethylene from the product stream is included for all of Examples A-C and Comparative Examples D-E. Said energy is expressed as kilowatt hour  
10 ("kWh"; 1 kWh = 3.6 megajoules) per kilogram (kg) of ethylene.

Table 4

| Ex. | Configuration                                                                              | kWh/kg of ethylene |
|-----|--------------------------------------------------------------------------------------------|--------------------|
| A   | air [O <sub>2</sub> +N <sub>2</sub> ] + PSA [0% methane rejection] + 1 distillation step   | 1.49               |
| B   | air [O <sub>2</sub> +N <sub>2</sub> ] + PSA [50% methane rejection] + 2 distillation steps | 1.93               |
| C   | air [O <sub>2</sub> +N <sub>2</sub> ] + PSA [100% methane rejection] + 1 distillation step | 1.62               |
| D*  | O <sub>2</sub> [no N <sub>2</sub> ] + distillation only [no PSA]                           | 2.62               |
| E*  | air [O <sub>2</sub> +N <sub>2</sub> ] + distillation only [no PSA]                         | 2.50               |

\* = comparative

15 From Table 4 above, it surprisingly appears that the energy needed to convert methane into ethylene and to separately recover methane and ethylene from the product stream is advantageously lowest in case the process of the present invention is carried out. That is, in all of Examples  
20 A, B and C, which exemplify the process of the present invention wherein in the OCM reaction step air is used and in the subsequent product separation step a sorption and desorption method (in said Examples: PSA method) is applied,

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said energy is advantageously lower than the energy needed to effect the same in those cases wherein a sorption and desorption method is not applied after the OCM reaction step, but only distillation steps are performed (as in Comparative Examples D and E), both when only oxygen (no nitrogen) is  
5 used in the OCM reaction step (Comparative Example D) and when air is used in the OCM reaction step (Comparative Example E).

Thus, surprisingly, this advantageous different energy  
10 effect obtained with the process of the present invention, as compared to the processes wherein only distillation steps are performed, is even obtained in cases where said sorption and desorption step is followed by 1 distillation step (Examples A and C) or 2 distillation steps (Example B) to recover the  
15 methane and ethylene.

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C L A I M S

1. Process for the oxidative coupling of methane to one or more C<sub>2</sub>+ hydrocarbons, comprising

a reaction step which comprises subjecting a gas stream comprising methane and air to methane oxidative coupling

5 conditions resulting in a gas stream comprising nitrogen, methane and ethylene;

a sorption step which comprises contacting the gas stream comprising nitrogen, methane and ethylene resulting from the reaction step with a sorption agent which has an affinity for  
10 nitrogen which is lower than that for methane which in turn is lower than that for ethylene, resulting in sorption of ethylene and optionally methane by the sorption agent and in a gas stream comprising nitrogen and optionally methane; and

a desorption step which comprises desorbing sorbed  
15 ethylene and optionally methane resulting in a gas stream comprising ethylene and optionally methane.

2. Process according to claim 1, wherein desorption in the desorption step is effected by reducing the pressure.

3. Process according to claim 2, wherein the pressure in the  
20 sorption step is in the range of from 5 to 30 bar, preferably 5 to 15 bar, more preferably 7 to 13 bar, and the pressure in the desorption step is in the range of from 0.1 to 3 bar, preferably 0.5 to 2 bar.

4. Process according to claim 3, wherein in the reaction  
25 step air is fed at a pressure in the range of from 5 to 15 bar, preferably 7 to 13 bar.

5. Process according to any one of the preceding claims, wherein the sorption step results in sorption of ethylene by the sorption agent and in a gas stream comprising nitrogen  
30 and methane; and the desorption step comprises desorbing

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sorbed ethylene resulting in a gas stream comprising ethylene.

6. Process according to claim 5, additionally comprising a distillation step which comprises distilling the gas stream comprising nitrogen and methane resulting from the sorption step, resulting in a top stream comprising nitrogen and a bottom stream comprising methane; and optionally a recycle step which comprises recycling the bottom stream comprising methane resulting from the distillation step to the reaction step.
7. Process according to any one of claims 1-4, wherein the sorption step results in sorption of ethylene and methane by the sorption agent and in a gas stream comprising nitrogen; and the desorption step comprises desorbing sorbed ethylene and methane resulting in a gas stream comprising ethylene and methane.
8. Process according to claim 7, additionally comprising a distillation step which comprises distilling the gas stream comprising ethylene and methane resulting from the desorption step, resulting in a top stream comprising methane and a bottom stream comprising ethylene; and optionally a recycle step which comprises recycling the top stream comprising methane resulting from the distillation step to the reaction step.

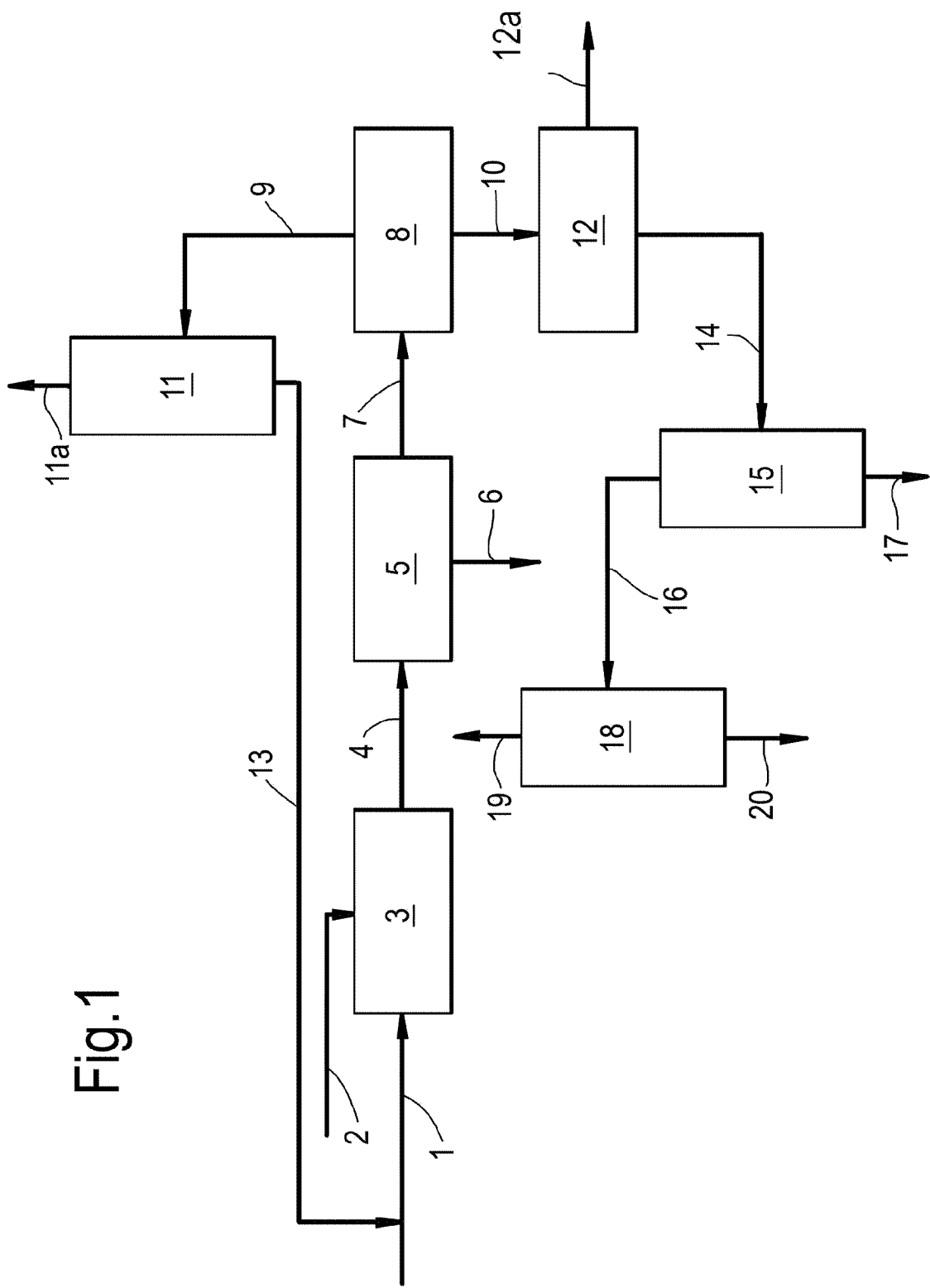


Fig.1

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/071939

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07C2/84 C07C7/04 C07C7/12  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 November 2016

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/071939

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                        |                       |
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International application No

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