



PCT

(10) International Publication Number
WO 2009/007436 A1

(43) International Publication Date
15 January 2009 (15.01.2009)

(51) International Patent Classification:

B01D 53/04 (2006.01) **C01B 21/04** (2006.01)
B01D 53/047 (2006.01) **C10L 3/10** (2006.01)
B01J 20/22 (2006.01)

(21) International Application Number:

PCT/EP2008/059048

(22) International Filing Date: 10 July 2008 (10.07.2008)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) Priority Data:

07112358.2 12 July 2007 (12.07.2007) EP

(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and

(75) **Inventors/Applicants (for US only): ELION, Wiveka, Jacoba** [NL/NL]; Carel van Bylandtlaan 16, NL-2596 HR The Hague (NL). **KAART, Sander** [NL/NL]; Carel van Bylandtlaan 16, NL-2596 HR The Hague (NL).

(74) Agent: SHELL INTERNATIONAL B.V.; Intellectual Property Services, PO Box 384, NL-2501 CJ The Hague (NL).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GO, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR SEPARATING NITROGEN FROM A MIXED NITROGEN AND METHANE CONTAINING STREAM BY USING A METAL ORGANIC FRAMEWORK

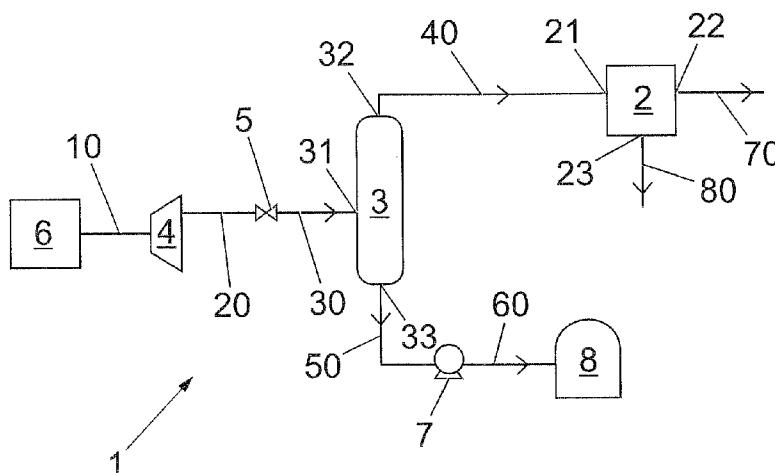


Fig. 3

(S7) Abstract: Method of separating nitrogen from a mixed nitrogen and methane-containing stream, the method at least comprising the step of contacting the mixed nitrogen and methane-containing stream (40) with a solid sorbent comprising a metal organic framework (2), thereby obtaining a nitrogen enriched stream (70). Optionally, the mixed nitrogen and methane-containing stream (40) is obtained from a gas/liquid separator (3) providing a gaseous methane-containing stream (40) and a liquid methane-containing stream (50), whilst at least a part of the gaseous methane-containing stream (40) is contacted with the solid sorbent in a MOF unit (2). As a further option, at least a part of the methane-containing stream (40) has been liquefied (6) upstream of the gas/liquid separator (3).



Published:

— *with international search report*

**METHOD AND APPARATUS FOR SEPARATING NITROGEN FROM A
MIXED NITROGEN AND METHANE CONTAINING STREAM BY USING A
METAL ORGANIC FRAMEWORK**

The present invention relates to a method for separating nitrogen from a mixed nitrogen and methane-containing stream, optionally derivable from liquefied natural gas (LNG).

5 Several processes and apparatuses for the removal of nitrogen from a methane-containing stream also comprising nitrogen, such as a flashed LNG stream, are known. One reason for removing nitrogen from such a stream may be in order to obtain natural gas having a desired gas quality,
10 e.g. a selected heating value (i.e. energy content when the gas is burned), according to gas specifications or the requirements of a consumer.

 An example of a known method for removing nitrogen from a methane-containing stream is disclosed in US Pat.
15 6,014,869. According to US Pat. 6,014,869, the amount of components having low boiling points such as nitrogen, hydrogen and helium in liquefied natural gas is reduced using a specific line-up including a fractionation column.

20 The fractionation column in US Pat. 6,014,869 provides a gas stream from its upper part which is enriched in components having low boiling points such as nitrogen. In some circumstances, there is not complete separation of the nitrogen and hydrocarbons, so that the
25 gas stream may also include a proportion of hydrocarbons such as methane. In such circumstances, it is possible for this gas stream to be used for example as a fuel stream. However, to be used as a fuel stream, the gas stream must first be compressed, which includes
30 compressing the proportion of the gas stream, which are components such as nitrogen, whose compression is

- 2 -

wasteful and serves no purpose as it is not usable as a fuel. Alternatively, the gas stream cannot simply be vented to atmosphere where it still has a proportion of one or more hydrocarbons such as methane.

5 Thus, subsequent use of the gas stream from the fractionation column in US Pat. 6,014,869 may not be efficient.

10 The present invention provides a method of separating nitrogen from a mixed nitrogen and methane-containing stream, the method at least comprising the step of:

- (a) providing a mixed nitrogen and methane-containing stream at a temperature of below -100 °C;
(b) contacting the mixed nitrogen and methane-containing stream with a solid sorbent comprising a metal organic framework, thereby obtaining a nitrogen enriched stream.
- 15

In a further aspect, the present invention provides an apparatus for separating nitrogen from a mixed nitrogen and methane-containing stream, the apparatus at least comprising:

- 20 - a source of a mixed nitrogen and methane-containing stream at a temperature of below -100 °C;
 - a MOF unit comprising a solid sorbent comprising a metal organic framework, and having at least one inlet for the mixed nitrogen and methane-containing stream and
25 at least one outlet for a nitrogen enriched stream.

Such an apparatus may be suitable for performing the method according to the present invention.

The apparatus may further comprise an outlet for a nitrogen-depleted stream.

30 The apparatus may further comprise a gas/liquid-separator upstream of the MOF unit. Further it is preferred that an inlet of the MOF unit can be connected to an outlet of the gas/liquid-separator for a gaseous methane-containing stream.

- 3 -

The apparatus may further comprise a liquefaction unit upstream of the gas/liquid separator. In this embodiment the apparatus preferably further comprises one or more expanders between the liquefaction unit and the gas/liquid separator.

Hereinafter the invention will be further illustrated by the following non-limiting drawings which show:

Figure 1 schematically a process scheme in accordance with one embodiment of the present invention;

Figure 2 schematically a process scheme in accordance with a second embodiment of the present invention;

Figure 3 schematically a process scheme in accordance with a third embodiment of the present invention;

Figure 4 schematically a process scheme in accordance with a fourth embodiment of the present invention;

Figure 5 shows graphs in a break-through experiment of an N₂ and CH₄ mixture through MOF-5 at -35 °C and 21 bar; and

Figure 5 shows graphs in a break-through experiment of an N₂ and CH₄ mixture through MOF-5 at -160 °C and 1 bar.

For the purpose of this description, a single reference number will be assigned to a line as well as a stream carried in that line. Same reference numbers refer to similar components.

The present disclosure proposes to employ a solid sorbent comprising a metal organic framework, which may be comprised in a MOF unit, for separating nitrogen from a mixed nitrogen and methane-containing stream. Metal organic framework materials are known in the art, and sometimes referred to with the acronym MOF as may be done in the present description and claims.

It has been found that using the surprisingly simple method and/or apparatus as outlined above, the highly efficient separation of one or more hydrocarbon components from the mixed stream, in particular methane,

- 4 -

allows the nitrogen enriched stream to be more easily disposed of, such as vented to atmosphere, without any or any significant, environmental concern.

5 The method and apparatus outlined above can be used, e.g. by regenerating the solid sorbent, to provide a nitrogen-depleted or hydrocarbon-enriched source of material for subsequent use. The nitrogen-depleted or hydrocarbon-enriched material can be used more efficiently than the original mixed stream. For example, 10 recompression of a nitrogen-depleted stream, such a stream comprising substantially of one or more hydrocarbons such as methane, can be more efficiently carried out without the inefficient co-compression of any significant nitrogen component. Any such recompressed 15 hydrocarbons can be used as, for example, a fuel or a hydrocarbon product, such as a compressed and optionally liquefied hydrocarbon stream such as liquefied natural gas (LNG).

20 In this way, the CAPEX and running costs for subsequently processing the nitrogen enriched stream, and preferably the nitrogen-depleted material, can be significantly lowered.

25 Further, also due to its simplicity and efficiency, the method according to the present invention, and the apparatus for performing the method, are expected to be very robust when compared with known line-ups.

30 Solid sorbents comprising a metal organic framework ("MOF") have significant functional flexibility, so that they can be designed for the particular adsorption and desorption required, especially for nitrogen.

35 The mixed nitrogen and methane-containing stream from which the nitrogen is to be separated may be any gaseous, liquid or partially condensed or vapourised methane-containing stream, and is suitably an LNG-derived stream. As is customary to the person skilled in the art, an LNG

- 5 -

stream may have various compositions. Usually an LNG stream to be vaporized is comprised substantially of methane, i.e. comprising at least 60-65 mol% methane. An LNG stream may comprise varying amounts of hydrocarbons heavier than methane, as well as other non-hydrocarbon compounds such as nitrogen, helium and hydrogen.

MOFs can be adapted to suit compound or substance-favouring adsorption. However, MOFs suitable for carrying out the method of the present invention at temperatures below 0°C, especially below -30°C, -100°C, -140°C, or even below -150°C, are particularly advantageous.

Depending on the source, the methane-containing stream may also contain varying amounts of compounds such as H₂O, CO₂, H₂S and other sulphur compounds, and the like. However, if the mixed nitrogen and methane-containing stream is a (previously) liquefied methane-containing stream such as LNG, these latter components usually have been previously substantially removed as they would otherwise freeze out during the liquefaction procedure. As the steps of liquefaction and removing undesired components such as H₂O, CO₂, and H₂S are well known to the person skilled in the art, they are not further discussed here.

Reduction or removal of any water may especially be desired, as water may cause deterioration of various types of MOFs. By removing of any water prior to contacting the natural gas with the solid sorbent, degradation of the metal organic framework can be reduced or even completely prevented. Removal of water may be performed using any suitable means, including glycol dehydration, contacting with calcium chloride, membrane systems or contacting with solid dessicants such as silica, silica gel, alumina, silica-alumina, activated carbon or molecular zeolite. Preferably, removal of water is done using a solid dessicant, especially a solid dessicant comprising

- 6 -

one or more of the following materials: zeolites, silica gel, activated alumina, activated carbon, calcium chloride, barium chloride and lithium chloride.

5 The solid sorbent comprising the metal organic framework may be provided the form of one or more solid sorbent beds, through which the mixed stream may be led. The solid sorbent comprising the metal organic framework may be provided in a MOF unit. A MOF unit is any suitable device, unit system or apparatus comprising one or more
10 vessels, beds, containers or units, each comprising one or more solid sorbents comprising MOF or MOF material being able to selectively adsorb one or more hydrocarbons from the mixed nitrogen and methane-containing stream. The person skilled in the art will understand that the
15 MOF unit can have many forms, including one or more vessels, etc, in series, parallel or both, comprising one or more layers or beds, optionally packed, of MOF material or materials.

For example, there may be at least one sorbent bed in
20 an adsorbing mode and at least one sorbent bed in a desorbing mode. Depending on the actual situation there may be combinations of two, three, four or even more sorbent beds, one in absorbing mode, the others in different stages of desorbing mode.

25 In general, a MOF unit can have an inlet for a feed fluid, an outlet for a depleted fluid, and optionally an inlet for any regeneration fluid and an outlet for any regeneration fluid enriched with the desorbed component. The depleted fluid usually has a lower boiling point than
30 the enriched regeneration fluid. The regeneration fluid or sweep fluid can also have a lower absolute value of heat of adsorption than component(s) to be desorbed. Regeneration preferably occurs counter-currently. A person skilled in the art is aware that co-current
35 regeneration is also possible.

- 7 -

Several solid sorbent MOF filled beds or vessels can provide an MOF unit to enable continuous flow of the various feed, depleted and enriched fluids. Timing of the cycling of the MOF beds or vessels can relate to the range of components that will be adsorbed on the MOFs.

Suitable MOFs or MOF materials are known in the art and described amongst others in EP-A-1,674,555, US 2003/0148165 A1 and US 2006/0185388 A1, the teaching of which is hereby specifically incorporated by reference. In particular, specific reference is made to the MOF materials as described in US 2006/0185388 A1, as well as to the methods for preparing the MOFs and to further references cited in US 2006/0185388 A1.

MOFs can be used as a powder but preferably the MOFs are used as shaped bodies such as extrudates or tablets. In general, MOFs comprise at least one metal ion, such as copper, zinc, etc, and at least one bidentate organic compound. Usually the MOF material is built up from a metal oxide, metal salt or metal cluster, and at least bidentate organic compounds, bound, preferably co-ordinatively bound, to said metal ion. MOF materials comprise accessible cavities. One cavity may be defined by eight metal ions linked together by at least bidentate organic compounds.

As to the metal component within the MOF material(s) for the present invention, particularly to be mentioned are the metal ions of the main group elements and of the subgroup elements of the periodic system of the elements, namely of the groups Ia, IIa, IIIa, IVa to VIIIa and Ib to VIb. References to the Periodic Table and groups thereof used herein refer to the previous IUPAC version of the Periodic Table of Elements such as that described in the 68th Edition of the Handbook of Chemistry and Physics (CRC Press). Among those metal components, particular reference is made to Mg, Ca, Sr, Ba, Sc, Y,

- 8 -

Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi, more preferably to Zn, Cu, Ni, Pd, Pt, Ru, Rh and Co, and most preferred Zn and Cu. For further information on metal ions in the MOF materials, reference is again made to US 2006/0185355 A1 and the cited references therein, in particular paragraphs [0031]-[0033] of US 2006/0185388 A1.

The at least one bidentate organic compound(s) can be any compound which is suitably co-ordinating. In practice, such a compound comprises at least one functional group capable for forming at least two coordination bonds with the metal ion. Said organic compound(s) thus usually have at least two centres, which are capable to coordinate the metal ions of a metal salt, oxide or cluster, etc, particularly with the metals of the aforementioned groups. With regard to the at least bidentate organic compound, specific mention is to be made of compounds as cited in paragraphs [0034]-[0052] of US 2006/0185388 A1.

Especially suitable bidentate organic compounds are compounds selected from the group of -COOH, -CS₂H, -NO₂, -B(OH)₂, -SO₃H, -Si(OH)₃, -Ge(OH)₃, -Sn(OH)₃, -Si(SH)₄, -Ge(SH)₄, -Sn(SH)₃, -PO₃H, -AsO₃H, -AsO₄H, -P(SH)₃, -As(SH)₃, -CH(RSH)₂, -C(RSH)₃, -CH(RNH₂)₂, -C(RNH₂)₃, -CH(ROH)₂, -C(ROH)₃, -CH(RCN)₂ and -C(RCN)₃, wherein R is preferably an alkylene group with 1 to 5 carbon atoms or an arylgroup.

Besides the at least bidentate organic compound (s), the framework material as used in accordance with the present invention may also comprise one or more monodentate ligand(s). Further examples and details regarding the at least bidentate organic compounds and the monodentate substances, from which the ligands of the MOFs may be derived, can be taken from EP-A 0 790 253,

- 9 -

EP-A-1,674,555 and US 2006/0185388 A1, whose respective content is incorporated into the present application by reference.

5 For the preparation of the MOFs, specific reference is made to paragraphs [0054]-[0102] of US 2006/0185388 A1, which is hereby incorporated by reference, as well as the further references cited therein.

10 By contacting the mixed nitrogen and methane-containing stream with solid sorbent comprising a metal organic framework, a nitrogen enriched stream and optionally, as described hereinafter, a nitrogen depleted stream, are obtained. In the present description and claims, the relative terms "nitrogen depleted" and "nitrogen enriched" indicate that the nitrogen content of
15 the streams removable from the solid sorbent is reduced or increased respectively, compared to the stream being contacting with the solid sorbent.

The person skilled in the art will readily understand that the nitrogen enriched stream may also be in enriched
20 in other low boiling components and/or low adsorbing components, such as helium and hydrogen, when compared to the stream just before contacting the solid sorbent.

Preferably the mixed nitrogen and methane-containing stream is obtained from a gas/liquid separator providing
25 a gaseous methane-containing stream and a liquid methane-containing stream. The gas/liquid separator may be any suitable means for obtaining at least a gaseous stream and a liquid stream, such as a scrubber, distillation column, etc. If desired, two or more gas/liquid
30 separators may be present. In one embodiment, at least a part of the gaseous methane-containing stream is contacted with the solid sorbent as the mixed nitrogen and methane-containing stream.

According to an especially preferred embodiment of
35 the present invention, at least a part of the mixed

- 10 -

nitrogen and methane-containing stream has been liquefied upstream of the gas/liquid separator. In this embodiment it is preferred that the liquefied methane-containing stream has been expanded one or more times before passing
5 into the gas/liquid separator. The person skilled in the art will understand that the expanding may be performed in various ways using any expansion device (e.g. using a throttling valve, a flash valve or a common expander).

Suitable nitrogen separation results can be obtained
10 where the MOF or MOF material has a BET surface area of greater than (>) 250 m²/gram, preferably >500 m²/gram, more preferably >1000 m²/gram, and most preferably >2000 m²/gram. For example MOF-5 has a BET of 2783 ± 40 m²/gram. BET surface area can be determined by
15 methods known in the art, such as N₂ adsorption at liquid nitrogen temperature using multipoint pressures of 0.08, 0.14 and 0.20 P/P₀ (relative pressure/vapour pressure), and using adsorption analyzers such as the TriStar 3000 apparatus of Micromeritics Instrument Corporation, USA.
20 BET surface area has been proposed and described by Brunauer, S., Emmett, P. H. & Teller, E. in "Adsorption of gases in multimolecular layers" *J. Am. Chem. Soc.* 60, pp. 309-319 (1938).

Another useful parameter to select a suitable MOF
25 material is the BET surface area expressed per volume of material rather than per unit of mass. This may be found by multiplying the BET surface area by a macroscopic density of the MOF material which may be the average density over a large volume relative to the volume of
30 the pores. The BET surface area per volume may be selected as high as possible, in order to provide an a large as possible surface area for a given solid sorbent bed size, or an as small as possible bed for a given desired surface area. Typically, the MOF or the MOF

- 11 -

material may be selected to have a BET surface area per liter exceeding 10^4 m²/liter, preferably exceeding 5×10^4 m²/liter. MOF-5, for example, may have a BET surface area of about 7×10^4 m²/liter or between 5×10^4 m²/liter and 10^5 m²/liter.

Further it is preferred that the solid sorbent comprises one or more MOF materials selected from the group consisting of: MOF-5, IRMOF-2, IRMOF-3, IRMOF-6, IRMOF-8, IRMOF-9, IRMOF-11, IRMOF-13, IRMOF-18, IRMOF-20, MOF-74, MOF-177, HKUST-1. All these materials are known in the art. The composition, suitable solvents and structural data for most of these and other MOF materials can be found in the Table in US 2006/0185388, which table is incorporated in the present description by reference. For example, MOF-5 comprises Zn²⁺ as a metal ion and ligands derived from terephthalic acid as the bidentate compound. An exemplary method for the preparation of MOF-5 is described in Example 1 of US 2003/0148165, which is hereby incorporated by reference.

The remaining examples are also described in literature. For example, synthesis of IRMOF-20; MOF-74; and HKUST-1 is described in J.L.L. Rowsell and Omar M. Yaghi, J. Am. Chem. Soc. 2006, Vol. 128, pp. 1304-1315.

Alternatively, the solid sorbent may comprise one or more MOF materials selected from the MIL group, e.g. comprising: MIL-53 and MIL-101, known from e.g. *Progress in Solid State Chemistry, Volume 33, Issues 2-4, 2005, Pages 187-197*, by C. Mellot-Draznieks and G. Férey.

Either after the nitrogen enriched stream has contacted with or been removed from the solid sorbent, or contemporaneously, adsorbed hydrocarbons can be desorbed to regenerate either all or part of the solid sorbent, (a part of the solid sorbent being in one or more separate beds, vessels or containers), thereby obtaining a nitrogen depleted stream. The person skilled in the art

- 12 -

understands that this desorption can be performed in many ways. Examples are described in the Handbook of Separation Process Technology, edited by R.W. Rousseau, 1987, Chapter 12, Adsorption, G.E. Keller II, R.A. Anderson, C.H. Jon, and 'Large-Scale Adsorption and Chromatography', Volumes 1-2 By: Wankat, Phillip C. 1986 Knovel, both of which are incorporated herein by reference.

The desorption may be carried out by PSA (pressure swing adsorption) or TSA (temperature swing adsorption), or a hybrid of both processes, which are described in EP 1 070 538 A2 and incorporated herein by reference. In general, changing the pressure and/or temperature beyond defined reference values leads to desorption rather than absorption. Also useable is rapid swing PSA. For the purpose of interpreting the present disclosure and claims, vacuum swing adsorption (VSA) is understood to be a form of pressure swing adsorption. It is useful in particular when the mixed nitrogen and methane-containing stream is at a pressure of about 1-2 bar.

As the person skilled in the art is familiar with how to perform a desorption process in general, and in particular TSA and PSA and PSA in the form of VSA, this is not further discussed here. Where hydrocarbons are adsorbed by the solid sorbent, then it is preferred - when using PSA and/or TSA - that the hydrocarbons are adsorbed at relatively high pressure and/or relatively low temperature compared to desorption, and desorbed at relatively low pressure and/or relatively high temperature compared to adsorption. However, even if the absorption pressure is low, PSA (possibly in the form of VSA) is preferred when it is desired to use the desorbing vapour as a fuel stream.

As described hereinbefore, the sorption of hydrocarbons on the solid sorbent can be reverted by

- 13 -

contacting said material with a stripping gas stream, regeneration fluid, sweep fluid, etc. Thereby, hydrocarbons are transferred from the sorbent to the stripping gas, etc., resulting in stripping gas loaded with hydrocarbons. Suitable stripping gases are for example inert gases or hydrocarbonaceous gases. For the purposes of the invention, it is preferred to use as a stripping gas a hydrocarbonaceous stream, especially purified natural gas. This is of particular relevance when using TSA, whereby the hydrocarbonaceous stream is essentially used to carry the heat to the sorbent.

The nitrogen depleted stream may have a temperature below 0°C, even below -30°C, -100°C, or lower, and may have a pressure of less than 10 bar, such as 1-2 bar.

In the present invention, it is possible for regeneration of the solid sorbent to be carried out continuously, thereby obtaining a continuous nitrogen depleted stream. Likewise, it is possible for the mixed nitrogen and methane-containing stream to be continuously contacted with the solid sorbent, thereby obtaining a continuous nitrogen enriched stream.

Figure 1 schematically shows a method of separating nitrogen from a mixed nitrogen and methane-containing stream. The mixed nitrogen and methane-containing stream 40 is passed to the inlet 21 of the MOF unit 2. As an example, the stream 40 comprises >15% or > 25 mol% nitrogen, such as between 30-60 mol% nitrogen.

The MOF unit 2 may be any suitable device, unit or apparatus comprising one or more beds, vessels, containers or units, each comprising one or more solid sorbents comprising one or more metal organic frameworks or MOF materials, being able to selectively adsorb one or more hydrocarbons from the mixed nitrogen and methane-containing stream 40. The person skilled in the art will understand that the MOF unit 2 can have many forms,

- 14 -

including one or more vessels, etc, in series, parallel or both, comprising one or more layers or beds, optionally packed, of MOF material or materials.

5 In the embodiment of Figure 1, the MOF unit 2 comprises three beds 42 each packed with a packing of MOF-5. During passing of the stream 40 through the MOF unit 2, at least a fraction of one or more hydrocarbons present in the stream 40 is adsorbed by the MOF material in the beds 42, whilst at least a major part of the
10 nitrogen phase is passed on and removed from the MOF unit 2 at outlet 22. This nitrogen enriched flow is collected as stream 70. Usually, the nitrogen enriched stream 70 contains >90, >95 or >98 mol% nitrogen, and as such can be vented to atmosphere.

15 Each bed 42 can be the same or different, and optionally contain the same or different MOF materials. The mixed nitrogen and methane-containing stream 40 may pass into the MOF unit 2 either intermittently or continuously. Independently, although usually in a
20 related manner, the nitrogen enriched stream 70 passes out of the MOF unit 2 through outlet 22 in an intermittent or continuous manner.

In Figure 1, a regeneration stream 90 also passes into the MOF unit 2 through inlet 24 in an intermittent
25 or continuous manner. The regeneration stream 90 is able to act upon the MOF material(s) in one or more of the beds 42 to get them to release the one or more hydrocarbons absorbed thereon, and so as to create an enriched regeneration stream 100 passing out of the MOF
30 unit 2 through outlet 25. The one or more hydrocarbons in the enriched regeneration stream 100 can be subsequently separated from the component or components of the regeneration stream 90 in a manner known in the art, to provide a nitrogen depleted stream.

- 15 -

The mixed nitrogen and methane-containing stream 40 is generally at a temperature of below 0°C. Where the mixed nitrogen and methane-containing stream 40 has a temperature below -100°C, for example below -140°C, -150°C or even -160°C, which will usually occur where the source of the mixed nitrogen and methane-containing stream 40 is an LNG stream 10, then the nitrogen enriched stream 70 will generally and preferably be at a temperature of below 0°C, typically below -100°C at least.

The mixed nitrogen and methane-containing stream 40 may be at a pressure of less than 10 bar, preferably between 1 and 2 bar such as is typically the case for LNG derived streams downstream of an end-flash system.

It is a benefit of the present invention that the MOF unit 2 can operate continuously, without requiring stop-start operation, for the provision of the nitrogen enriched stream 70. Continuous operation still encompasses variation in the various flows therethrough which may vary between 0-100%. Continuous operation can be aided by the regeneration stream 90 acting up on one or more of the MOF beds 42 having absorbed hydrocarbons in a sequential or cyclical manner, in rotation with the mixed stream 40 passing to one or more other MOF beds 42 not so absorbed, for example after having been regenerated.

Figure 2 shows a second arrangement of the MOF unit 2, wherein the mixed nitrogen and methane-containing stream 40 passes into a first manifold 15 able to direct the mixed stream 40 either solely or in fractions through one or more of three MOF beds 42 through first conduits 17. After contact with the relevant solid sorbent comprising a metal organic framework in the MOF beds 42, the resultant stream passes by a second conduit 18 into a second manifold 16, to be collected and

- 16 -

provided as a single nitrogen enriched stream 70 in a manner described herein above through outlet 22.

Similarly, a regeneration stream 90 can pass through inlet 24 into the second manifold 16, and be directed either solely or fractionally through one or more of the MOF beds 42 through the second conduits 18, then through the first conduits 17 and be directed by the first manifold 15 to provide through outlet 25 the enriched regeneration steam 100.

Figure 2 illustrates the possibility for one of more of the MOF beds 42 to be supplied with mixed stream 40, whilst one or more other MOF beds 42 is supplied with the regeneration stream 90. Thus, continuous operation is possible wherein one or more of the MOF beds 42 are separating nitrogen from the mixed nitrogen and methane-containing stream 40, whilst one or more other MOF beds 42 are being regenerated. The first and second manifolds 15, 16 allow switching of streams to and from each MOF bed 42 through first and second conduits 17, 18 in a suitable manner to allow such operation.

Figure 3 schematically shows a process scheme (generally indicated with reference no. 1) for the separation of nitrogen from a mixed nitrogen and methane-containing stream derived from an LNG stream, whereby a nitrogen depleted LNG stream is obtained having a higher heating value.

The process scheme of Figure 3 comprises the MOF unit 2 comprising one or more solid sorbents comprising a metal organic framework, a gas/liquid separator 3, an expander 4 and a Joule-Thomson valve 5, a liquefaction unit 6 comprising one or more heat exchangers with associated refrigerant circuits (not shown), a pump 7 and an LNG storage tank 8. The person skilled in the art will readily understand that further elements may be present if desired.

- 17 -

During use of the embodiment as shown in Figure 3, an LNG stream 10 as produced in the liquefaction unit 6 is expanded in the expander 4 (stream 20) and then in the Joule-Thomson valve 5, thereby obtaining a partly condensed LNG stream 30 that is subsequently fed into a gas/liquid separator 3 (such as an "end flash vessel") at inlet 31. Typically, the inlet pressure to the gas/liquid separator 3 will be between 0.5 and 10 bar, preferably between 1 and 5 bar and more preferably between 1 and 2 bar. The inlet temperature to the gas/liquid separator 3 will usually be between -140 °C and -165 °C. The LNG stream in line 10 can comprise approximately the following composition: >80 mol% methane and >1 mol% N₂.

In the gas/liquid separator 3, the partially condensed stream 30 is separated into a gaseous overhead stream (removed at outlet 32) and a liquid bottom stream 50 (removed at outlet 33).

The liquid bottom stream 50 is usually enriched in methane relative to the stream 30, and comprises the majority of the LNG stream 30. The liquid bottom stream 50 can be pumped as stream 60 to the LNG storage tank 8 using the pump 7. In the tank 8 the LNG is temporarily stored. In case the apparatus 1 is situated on an LNG exporting terminal, the LNG stored in the tank may be subsequently loaded into a transport vessel (not shown) before it is transported overseas. In case the apparatus 1 forms part of a regasification terminal (at an LNG import location where the LNG is usually supplied by a transport vessel rather than a liquefaction unit 6), the LNG in the tank 8 may be subsequently passed to a vaporizer (not shown).

Due to the action of the gas/liquid separator 3, nitrogen in the stream 30 favours passing upwardly out through the outlet 32. Thus, the gaseous overhead stream removed at the outlet 32 of the separator 3 is provided

- 18 -

as a mixed nitrogen and methane-containing stream 40, which will typically be at a temperature close to the inlet temperature to the gas/liquid separator 3. This stream 40 is passed to the inlet 21 of the MOF unit 2.

5 Usually the stream 40 comprises >15% or > 25 mol% nitrogen, such as between 30-60 mol% nitrogen.

During passing of the stream 40 through the MOF unit 2, at least a fraction of one or more hydrocarbons, in particular methane, present in the stream 40 is adsorbed
10 by the MOF material in the MOF unit 2, whilst at least a major part of the nitrogen phase is passed on and removed from the MOF unit 2 at outlet 22. This nitrogen enriched flow is collected as stream 70.

Either after the nitrogen enriched stream has been
15 collected as stream 70 or contemporaneously therewith as described hereinbefore, the hydrocarbons adsorbed in the MOF material in the MOF unit 2 can be desorbed. This may be done by using for example PSA, TSA, a hybrid of these processes, or any other suitable desorbing technique,
20 usually involving a sweep gas, regeneration stream/gas, etc., to remove the desorbed hydrocarbons from the MOF material. The desorbed hydrocarbons are removed at outlet 23 and are collected either directly or after separation from the sweep gas as a nitrogen depleted stream 80.

25 Stream 80 may be used as fuel. Alternatively, stream 80 may be recombined with the LNG stream 50, optionally after first compressing and re-liquefying stream 80.

The person skilled in the art will understand that the outlets 22 and 23 may be separate outlets or one and
30 the same outlet. Further, the person skilled in the art will understand that instead of one MOF unit 2, several parallel MOF units may be used. Also, several MOF units (containing different MOF materials) may be placed in series to enable the separation of one or more other
35 streams (including nitrogen).

- 19 -

Cold recovery from the nitrogen enriched stream 70 and/or the nitrogen-depleted stream 80 can be effected in a manner known in the art.

For example, Figure 4 shows a second arrangement (generally indicated with reference no. 2) where the mixed nitrogen and methane-containing stream 40 passes into the MOF unit 2 to provide a nitrogen enriched stream 70 which passes into a first cold recovery unit 44, prior to being vented to atmosphere as stream 70a. Meanwhile the nitrogen depleted stream 80 passes through a second cold recovery unit 46 to provide a warmed stream 80a, which then passes through a compressor 48 to provide a compressed methane-containing hydrocarbon stream 80b, which could be used as fuel gas, or even recycled into a hydrocarbon liquefaction plant (not shown). This results in a saving on compression power and capacity, as the inert nitrogen components of stream 40 need not be compressed together with the hydrocarbon components.

Where the MOF unit 2 is placed directly after the gas/liquid separator 3, the conditions of the natural gas vapour absorbed on the MOF material in the MOF unit 2 (for example 1 bar and -160°C), may prefer the TSA technique for desorption in the MOF unit 2. The cold energy of the nitrogen-enriched stream 70 (shown in Figure 4) can be used for the process, after which it can be vented to atmosphere. At the same time methane will be adsorbed on the MOF bed.

The present invention is further advantageous as the re-liquefaction of the desorbed hydrocarbon(s) such as methane requires less power than prior art processes, as cryogenic separation of any nitrogen therewith is no longer needed.

In a first alternative embodiment to the arrangement shown in Figure 1, the MOF unit 2 may be located prior to the gas/liquid separator 3 so as to separate nitrogen

- 20 -

from a mixed nitrogen and methane-containing stream, generally obtained directly from expansion or expansions of a liquefied methane-containing hydrocarbon stream such as LNG.

5 In a second alternative embodiment of the arrangement shown in the accompanying figures, the MOF unit 2 may be located in the path of any gaseous hydrocarbon stream with a high concentration of nitrogen, including such a stream at a high pressure (for example <70 bar).

10 Bench scale gas separation experiments have been performed to investigate the separation of nitrogen from a mixed stream consisting of 35 mol.% nitrogen and 65 mol.% methane, using MOF-5.

 The MOF-5 was produced by placing 10.3 g (61.9 mmol) of terephthalic acid (98%, obtained from Merck) and 49.0 g (187.5 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98.5 % obtained from Merck) in a round bottomed flask of 2 liter, which was equipped with a stirring bar and a reflux condenser, and connected to an argon Schlenk line. The reactants were dissolved in 1415 g of N,N-diethylformamide (DEF, 99% obtained from Merck) and the solution was heated under static argon to 105 °C for 24 hours while slowly stirring. Light yellow crystals were formed. The contents of the flask were allowed to cool down to ambient temperature and the slurry was subsequently filtered using a P4 glass filter. Next, the residue on the filter was washed four times with 100 ml of N,N-dimethylformamide (DMF, obtained under the name Suprasolv, Merck) and four times with 100 ml CHCl_3 (obtained from Merck under the name Suprasolv). The washed sample was dried at room temperature and reduced pressure and subsequently transferred to a Soxhlet tube, which had been dried by overnight evacuation at 90 °C. Soxhlet extraction was performed with 250 ml CHCl_3 and

- 21 -

under argon atmosphere. In total, approximately 160
siphons took place during 20 hours. Finally, the product
(approx. 13 g) was collected from the Soxhlet tube,
transferred to a Schlenk tube and evacuated overnight at
5 150 °C. The content of the Schlenk tube was transferred
to a glass bottle under argon atmosphere.

A stainless steel pipe with a 9 mm internal diameter
was filled with between about 1 gram and 3 grams of the
solvent-free MOF-5 and a portion of between about 1 and 3
10 grams of de-activated SiC, which had been de-activated
first by overnight heating at 500 °C. The average
particle size of the SiC and the MOF-5 particles was
about 0.5 mm. The SiC was applied to improve heat
transfer from a heating/cooling mantle to the gas mixture
and to obtain a desired flow profile. The pressure was
15 controlled by means of a back pressure regulator and the
gas flow by means of mass flow controllers. The precise
flows were determined with a soap bubble flow meter, and
corrected for the actual temperature and pressure by
20 applying the ideal gas law. Gas composition downstream of
the tube was verified using a gas chromatograph (GC)
equipped with a thermo-conduct detector (TCD).

The tube was placed vertically, which would usually
be the case in commercial applications as well.
25 Adsorption was carried out by leading the gas mixture
through the tube in upward direction. Prior to the start
of any experiment, the MOF-5 bed was filled with He to
the pressure at which the adsorption would be carried
out.

30 Figures 5 and 6 show graphs of so-called break-
through curves plotting gas chromatograph signals (in
area counts) for nitrogen (square data points connected
by line 95) and methane (triangular data points connected
by line 96) downstream of the MOF-5 bed as a function of
35 admitted gas mixture upstream of the MOF-5 bed in kg of

- 22 -

the gas mixture per cubic meter. The data of Figure 5 was obtained at a temperature of -35 °C and a pressure of 21 bar, and it can be seen that separation is quite poor at this temperature. Figure 6 was measured at -160 °C and a
5 pressure of 1 bar, which correspond to typical conditions directly after an end flash vessel. It can be concluded that the nitrogen/methane separation is much better than in the experiment of Figure 5.

10 The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention.

- 23 -

C L A I M S

1. Method of separating nitrogen from a mixed nitrogen and methane-containing stream, the method at least comprising the step of:
 - (a) providing a mixed nitrogen and methane-containing stream at a temperature of below -100 °C;
 - (b) contacting the mixed nitrogen and methane-containing stream with a solid sorbent comprising a metal organic framework, thereby obtaining a nitrogen enriched stream.
2. Method according to claim 1, wherein the mixed nitrogen and methane-containing stream is obtained from a gas/liquid separator providing a gaseous methane-containing stream, and a liquid methane-containing stream, preferably LNG.
3. Method according to claim 2, wherein at least a part of the gaseous methane-containing stream is contacted with the solid sorbent as the mixed nitrogen and methane-containing stream.
4. Method according to one or more of the preceding claims, wherein the mixed nitrogen and methane-containing stream is at a temperature of below -140 °C.
5. Method according to one or more of the preceding claims, wherein the mixed nitrogen and methane-containing stream is and at a pressure of less than 10 bar.
6. Method according to one or more of the preceding claims 2 to 5, wherein at least a part of the mixed nitrogen and methane-containing stream has been liquefied upstream of the gas/liquid separator.
7. Method according to one or more of the preceding claims, wherein the metal organic framework has a BET surface area of >500 m²/gram.
8. Method according to any one of the preceding claims, wherein the metal organic framework comprises at least

- 24 -

one metal ion and at least one bidentate organic compound, wherein the bidentate organic compound is bound to the metal ion.

- 5 9. Method according to one or more of the preceding claims, wherein the solid sorbent comprises one or more metal organic frameworks selected from the group consisting of: MOF-5, IRMOF-2, IRMOF-3, IRMOF-6, IRMOF-8, IRMOF-9, IRMOF-11, IRMOF-13, IRMOF-18, IRMOF-20, MOF-74, MOF-177, HKUST-1, MIL-53, MIL-101.
- 10 10. Method according to one or more of the preceding claims, wherein during contacting of the mixed nitrogen and methane-containing stream with the solid sorbent, at least a fraction of the methane molecules in the mixed stream is adsorbed.
- 15 11. Method according to one or more of the preceding claims further comprising the step of:
(c) regenerating the solid sorbent to provide a nitrogen depleted stream.
- 20 12. Method according to claim 11, wherein the regenerating causes desorbing of at least a fraction of the adsorbed number of methane molecules, thereby obtaining the nitrogen depleted stream.
- 25 13. Method according to claim 11 or claim 12, wherein the regenerating is provided by one or more of the group comprising: pressure swing adsorption and temperature swing adsorption.
- 30 14. Apparatus for separating nitrogen from a mixed nitrogen and methane-containing stream, the apparatus at least comprising:
- a source of a mixed nitrogen and methane-containing stream at a temperature of below -100 °C;
- a MOF unit comprising a solid sorbent comprising a metal organic framework, and having at least one inlet for the mixed nitrogen and methane-containing stream and
35 at least one outlet for a nitrogen enriched stream.

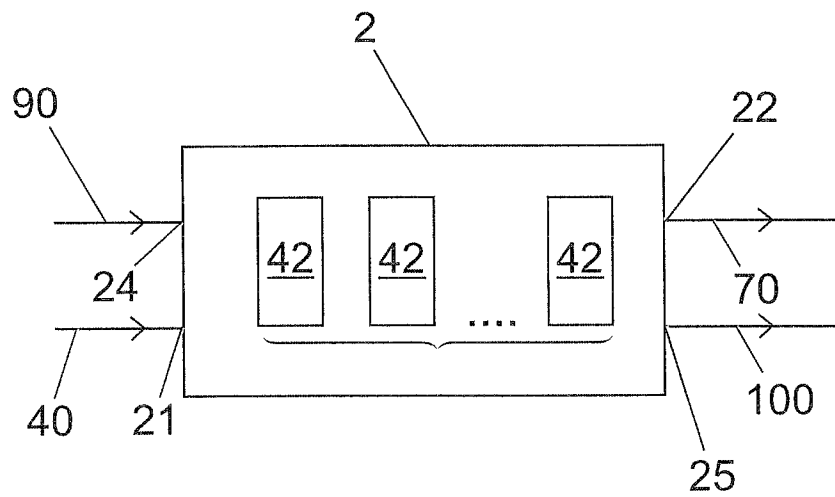
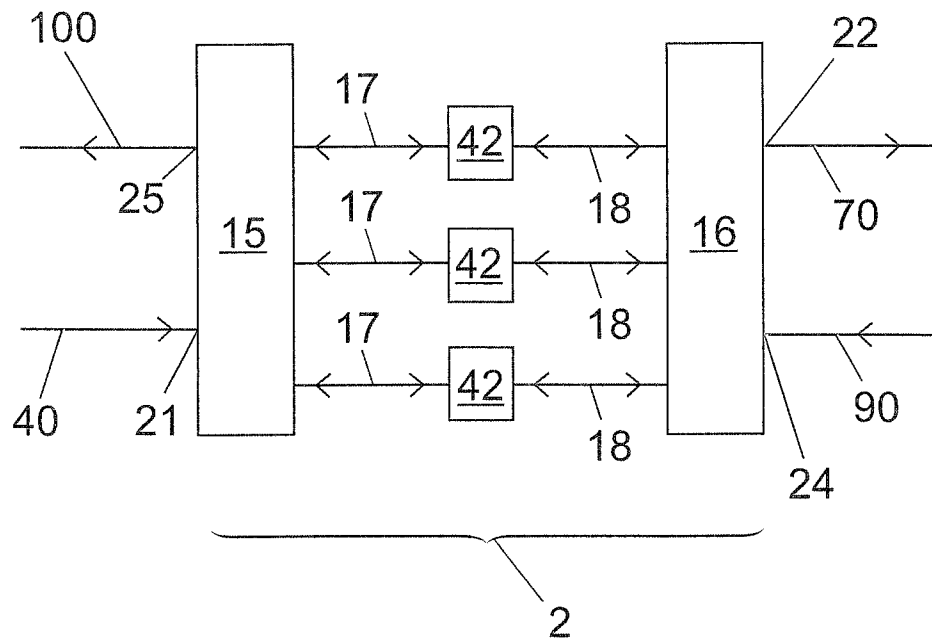
- 25 -

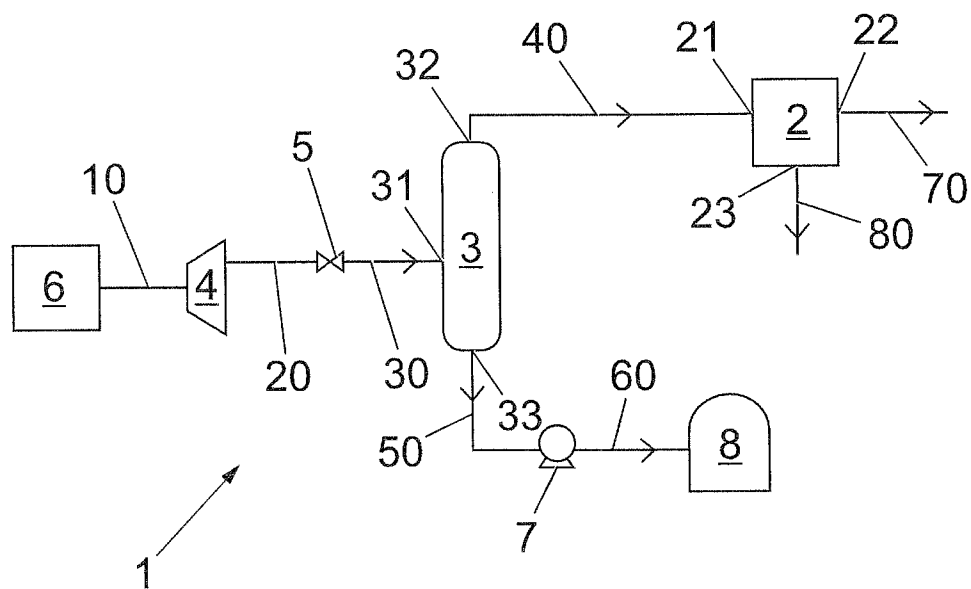
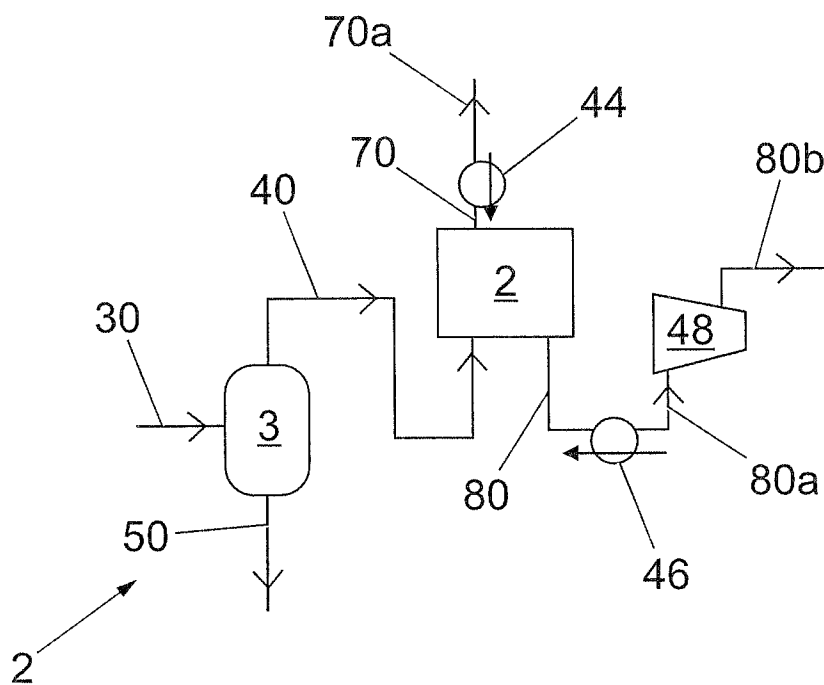
15. Apparatus according to claim 14, wherein the source of the mixed nitrogen and methane-containing stream comprises a gas/liquid separator.

5 16. Apparatus according claim 14 or claim 15, wherein the source of the mixed nitrogen and methane-containing stream comprises a liquefaction unit.

17. Apparatus according to any one of claims 14 to 16, further comprising:

- 10 - regenerator means for regenerating the solid sorbent;
and
- at least one outlet for a nitrogen-depleted stream.

*Fig. 1**Fig. 2*

*Fig. 3**Fig. 4*

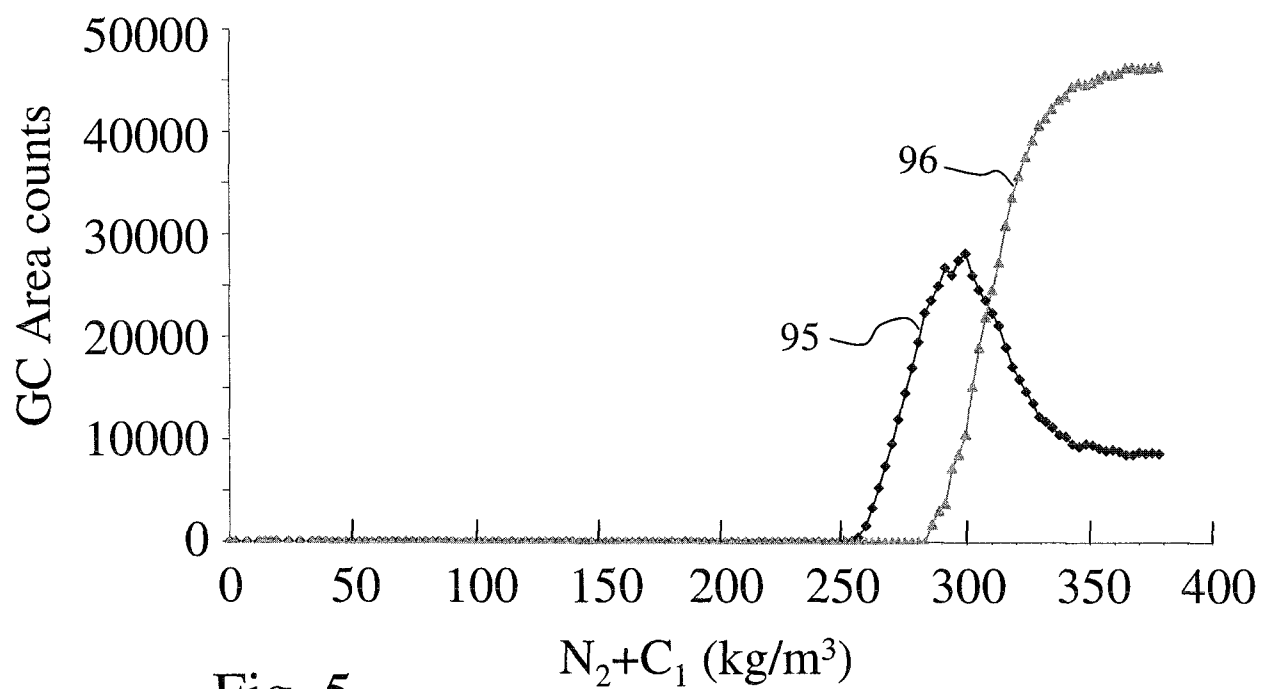


Fig. 5

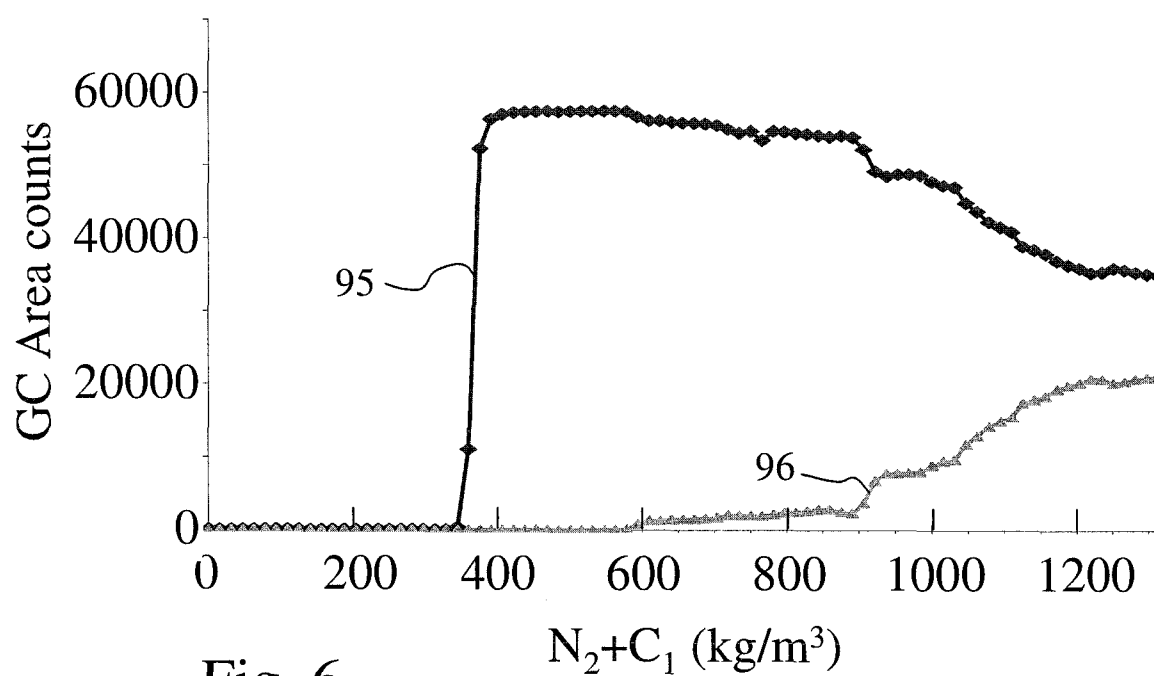


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/059048

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D53/04 B01D53/047 B01J20/22 C01B21/04 C10L3/10		
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) B01J B01D C01B C10L		
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 practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/045030 A1 (TONKOVICH ANNA-LEE [US] ET AL TONKOVICH ANNA LEE [US] ET AL) 3 March 2005 (2005-03-03) claims 1-3,5,6,28,51; figure 2 paragraphs [0003], [0015] - [0017], [0079], [0081], [0082], [0132]	1,14
Y	US 6 631 626 B1 (HAHN PAUL R [US]) 14 October 2003 (2003-10-14)	1-17
Y	column 5, line 31 - line 59 column 10, lines 5-20; figures 1,2 column 11, line 44 - column 13, line 32 column 13, line 33 - line 44	1-17
Y	JP 2003 342260 A (OSAKA GAS CO LTD) 3 December 2003 (2003-12-03) paragraphs [0002] - [0004]; claims 1,3,7 -/--	1-17
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *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. *8* document member of the same patent family		
Date of the actual completion of the international search 15 October 2008		Date of mailing of the international search report 24/10/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Burkhardt, Thorsten

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/059048

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT.

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	& DATABASE WPI Week 200412 Thomson Scientific, London, GB; AN 2004-113023 & JP 2003 342260 A (OSAKA GAS CO LTD) 3 December 2003 (2003-12-03) abstract ----- WO 2005/049484 A (BASF AG [DE]; MUELLER ULRICH [DE]) 2 June 2005 (2005-06-02) claims 1-6 page 1, line 7 - line 17 page 3, line 6 - line 12 page 4, line 29 - page 5, line 24 page 23, line 14 - page 24, line 16 page 33, line 19 - line 29 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/059048

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2005045030	A1	03-03-2005	NONE	
US 6631626	B1	14-10-2003	AU 2003254222 A1	25-02-2004
			EG 23917 A	30-12-2007
			RU 2300061 C2	27-05-2007
			WO 2004015346 A1	19-02-2004
JP 2003342260	A	03-12-2003	NONE	
WO 2005049484	A	02-06-2005	CA 2544859 A1	02-06-2005
			CA 2546327 A1	02-06-2005
			CN 1886536 A	27-12-2006
			CN 1886334 A	27-12-2006
			DE 10355087 A1	09-06-2005
			EP 1689670 A1	16-08-2006
			EP 1687462 A1	09-08-2006
			WO 2005049892 A1	02-06-2005
			JP 2007533846 T	22-11-2007
			JP 2007534896 T	29-11-2007
			KR 20070013261 A	30-01-2007
			KR 20060111618 A	27-10-2006
			US 2007227898 A1	04-10-2007