



(51) International Patent Classification:

B01D 53/04 (2006.01) **C10K 1/32** (2006.01)
B01D 53/047 (2006.01) **C01B 3/56** (2006.01)

(21) International Application Number:

PCT/EP2012/071188

(22) International Filing Date:

25 October 2012 (25.10.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11186512.7 25 October 2011 (25.10.2011) EP
11186516.8 25 October 2011 (25.10.2011) 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).

(71) Applicant (for US only): **SHELL OIL COMPANY** [US/US]; PO Box 2463, One Shell Plaza, Houston, Texas 77252-2463 (US).

(72) Inventors: **TE BRAAKE, Justus Theodorus Gerardus**; Grasweg 31, NL-1031 HW Amsterdam (NL). **BRACHT, Maarten**; Grasweg 31, NL-1031 HW Amsterdam (NL). **BUNGKU, Desmond Andrew**; Grasweg 31, NL-1031 HW Amsterdam (NL). **VAN DE GRAAF, Wouter David**;

Grasweg 31, NL-1031 HW Amsterdam (NL). **LINDERS, Xander**; Grasweg 31, NL-1031 HW Amsterdam (NL). **SADASIVAN VIJAYAKUMARI, Sivakumar**; Grasweg 31, NL-1031 HW Amsterdam (NL).

(74) Agent: **MATTHEZING, Robert Maarten**; 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, BN, BR, BW, BY, BZ, CA, CH, CL, 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, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD FOR PROCESSING FISCHER-TROPSCH OFF-GAS

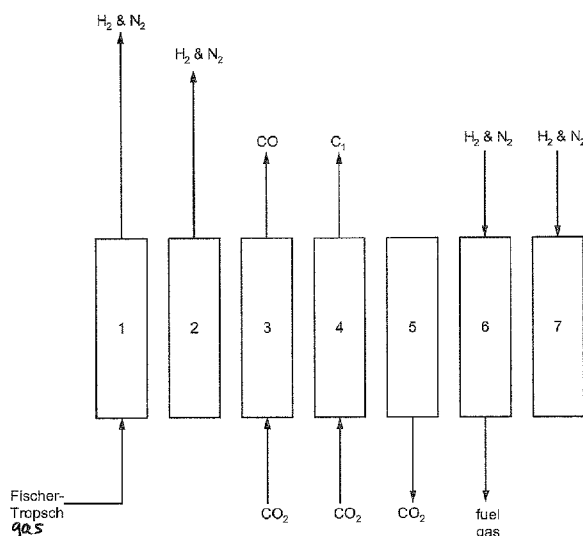


FIG. 1 A

(57) Abstract: This invention concerns a method for producing a gas comprising at least 80 vol% carbon monoxide from a Fischer-Tropsch off-gas. The method comprises the following steps: (1) feeding Fischer-Tropsch off-gas through a column comprising an adsorbent bed at high pressure and discharging effluent; (2) reducing the pressure in the column and the bed slightly; (3) rinsing the column and the adsorbent bed with methane or carbon dioxide; (4) rinsing the column and the adsorbent bed with carbon dioxide; (5) reducing the pressure of the column and adsorbent bed to a low pressure; (6) rinsing the column and adsorbent bed with a mixture of hydrogen and nitrogen; (7) pressurizing the column and adsorbent bed to a high pressure again using a mixture of hydrogen and nitrogen. The carbon monoxide rich product stream obtained in step (3) can be sent as feed to a Fischer-Tropsch reaction. Step (4) produces a methane stream comprising at least 80 vol% methane. In a preferred embodiment a gas comprising at least 80 vol% hydrogen is produced as well.



Declarations under Rule 4.17:

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

Published:

— *with international search report (Art. 21(3))*

METHOD FOR PROCESSING FISCHER-TROPSCH OFF-GAS

Field of the Invention

The present invention relates to a process for processing Fischer-Tropsch off-gas. Unconverted carbon monoxide is recovered from the Fischer-Tropsch off-gas. In some embodiments unconverted carbon monoxide as well as unconverted hydrogen are recovered from the Fischer-Tropsch off-gas.

The invention especially relates to a process in which recycling of unconverted carbon monoxide, and optionally unconverted hydrogen, to one or more Fischer-Tropsch reactors is optimized.

Background of the Invention

The Fischer-Tropsch process can be used for the conversion of hydrocarbonaceous feed stocks into normally liquid and/or solid hydrocarbons (i.e. measured at 0°C, 1 bar). The feed stock (e.g. natural gas, associated gas, coal-bed methane, residual oil fractions, biomass and/or coal) is converted in a first step into a mixture of hydrogen and carbon monoxide. This mixture is often referred to as synthesis gas or syngas. The synthesis gas is fed into a reactor where it is converted over a suitable catalyst at elevated temperature and pressure into paraffinic compounds ranging from methane to high molecular weight molecules comprising up to 200 carbon atoms, or, under particular circumstances, even more.

5

10

15

20

25

The hydrocarbon products manufactured in the Fischer-Tropsch process are processed into different fractions, for example a liquid hydrocarbon stream comprising mainly C₅+ hydrocarbons, and a gaseous hydrocarbon stream which comprises methane, carbon dioxide, unconverted carbon monoxide, unconverted hydrogen, and lower hydrocarbons. The gaseous hydrocarbon stream may also comprise nitrogen as the syngas sent to the Fischer-Tropsch reactor may contain some nitrogen.

The gaseous hydrocarbon stream is often referred to as Fischer-Tropsch off-gas. Fischer-Tropsch off-gas can be recycled to the syngas manufacturing or to the Fischer-Tropsch reactor. Sometimes lower hydrocarbons are removed before the off-gas is recycled. Lower hydrocarbons may be removed by decreasing the temperature of the off-gas and then applying a gas-liquid separation. However, when the off-gas is recycled to the syngas manufacturing or to the Fischer-Tropsch reactor, the components in the off-gas which do not take part in the Fischer-Tropsch reaction, such as carbon dioxide, nitrogen and methane, occupy reactor space. The components which do not take part in the Fischer-Tropsch reaction are also referred to as "inerts".

The level of inerts in the Fischer-Tropsch reactor increases with increasing Fischer-Tropsch off-gas recycling. The pace of the build-up of inerts can be reduced by treating the off-gas before it is recycled. When the off-gas is passed through a pressure swing adsorption unit (PSA), it is normally possible to remove carbon dioxide and water from the off-gas. It is often possible to recover a hydrogen stream from the off-gas by means of a PSA unit; the hydrogen stream can be recycled to the Fischer-Tropsch reactor. Nevertheless, common

commercial PSA units are often not designed to recover a carbon monoxide stream. And some common commercial PSA units result in a hydrogen stream comprising a significant amount of nitrogen. Therefore it is common to recycle only a relatively small part of the off-gas. One possibility is to recycle a part of the Fischer-Tropsch off-gas to one or more Fischer-Tropsch reactors while another part of the off-gas is used as fuel. A downside of this is that only a part of the carbon atoms of the hydrocarbonaceous feed stock is converted to the desired C₅+ hydrocarbons.

US5112590 and US5096470 describe the separation of gases using specific PSA systems with a first PSA unit for producing hydrogen and a second PSA unit for producing carbon monoxide. Such systems may be useful for gas mixtures comprising a relatively high amount of hydrogen. Such systems are, however, not suitable for gas mixtures comprising a relatively low amount of hydrogen, e.g. less than 50 volume % calculated on the total gas mixture. Furthermore, in case of a gas feed comprising a significant amount of nitrogen such systems will not result in the product cuts as described. When, for example, pure hydrogen would be separated using the first PSA, nitrogen would contaminate the intermediate carbon monoxide stream in a system according to US5112590 or US5096470. The systems of US5112590 and US5096470 may therefore be suitable to treat a hydrogen-rich gas mixture exiting a steam methane reformer, but they are not suitable to treat a nitrogen-comprising hydrogen-lean off-gas of a Fischer-Tropsch process.

US20110011128 describes a PSA comprising system in which purified hydrogen is produced using a PSA, which may be a conventional co-purge H₂ PSA unit. Such a system

may be useful to a hydrogen-rich gas mixture exiting a steam methane reformer, but is not suitable to treat nitrogen comprising hydrogen-lean off-gas of a Fischer-Tropsch process.

5 US20040077736 mentions a process in which a liquid phase and a vapour phase are withdrawn from a hydrocarbons synthesis stage. In a vapour phase work-up stage, hydrocarbon products having 3 or more carbon atoms may be removed and the residual vapour phase may then
10 pass to a PSA. Using the PSA first, second and optionally third gas components are separated. The first gas component comprises carbon monoxide and hydrogen. The second gas component comprises methane, and the optional third gas component comprises carbon dioxide. The first
15 gas component is recycled to the hydrocarbon synthesis stage. US20040077736 does not provide details on the method PSA method used. A regular use of a normal PSA would result in a relatively low recovery of carbon monoxide in the first gas component, and a build-up of
20 nitrogen in the reactor upon recycling the first gas component to the hydrocarbon synthesis stage.

US20080300326-A1 describes the use of a PSA method to separate Fischer-Tropsch off-gas. The method produces at least one gas stream comprising hydrogen, at least one
25 gas stream mainly comprising methane, and at least one gas stream comprising carbon dioxide, nitrogen and/or argon, and hydrocarbons with at least 2 carbon atoms. The PSA used comprises at least three adsorbent beds: alumina, carbon molecular sieves or silicates, activated
30 carbon, and optionally zeolite. The alumina is used to remove water. The carbon molecular sieves or silicates are used to adsorb carbon dioxide and partially methane. The activated carbon is used to adsorb methane and

partially nitrogen and carbon monoxide. Zeolite may be used to adsorb nitrogen, argon and carbon monoxide. The product stream of the PSA mainly comprises hydrogen. The other gas streams are obtained during the decompression phase. Disadvantages of the method of US20080300326-A1 are at least the following. Nitrogen is only partially adsorbed in the PSA. This results in a build-up of nitrogen in the Fischer-Tropsch reactor when the hydrogen stream is used as reactant gas. Also the methane stream comprises nitrogen and thus results in the build-up of nitrogen in the syngas, and thus in the Fischer-Tropsch reactor, when the methane stream is used for generating syngas. Another disadvantage of the method of US20080300326-A1 is that carbon monoxide is only recycled to the Fischer-Tropsch reactor in a limited amount. Carbon monoxide is present in the hydrogen stream and in the methane stream. Nevertheless, at least 50% of the CO initially present in the off-gas ends up in the third stream which is used as fuel.

There is a desire to obtain a pure carbon monoxide stream from Fischer-Tropsch off-gas. Such a pure carbon monoxide stream can then be recycled to the Fischer-Tropsch reactor. This would make it possible to convert most of the carbon atoms of the hydrocarbonaceous feed stock to the desired C₅+ hydrocarbons. It is even more desired to additionally obtain a pure hydrogen stream from Fischer-Tropsch off-gas, which may also be recycled to the Fischer-Tropsch reactor.

Summary of the Invention

The invention provides a method for producing a gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of the gas, from a gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon

monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, said method comprising, in sequence, the following steps:

- 5 (1) feeding a gas mixture through a column comprising an adsorbent bed, said gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture,
 - 10 - with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure hydrogen, or with a mixture of hydrogen and nitrogen, and
 - 15 - discharging effluent from the other end of said bed, and
 - continuing said feeding and said discharging until a carbon monoxide comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated
 - 20 from the end of the bed at which the gas mixture is being fed; and
- (2) ceasing the feeding of the gas mixture comprising methane, carbon dioxide, carbon monoxide and hydrogen, and reducing the pressure in the column and the bed with about 5 to 10
- 25 bar a; and
- (3) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon dioxide, through the column and adsorbent bed,
- 30 - the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and

- discharging effluent from the other end of said bed, and
 - continuing said feeding and said discharging until at least 60% of the carbon monoxide that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- 5
- (4) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% carbon dioxide through the column and adsorbent bed,
- 10
- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
 - discharging effluent from the other end of said bed, and
 - continuing said feeding and said discharging until at least 60% of the methane that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- 15
- (5) ceasing the feeding of a gas comprising at least 95
- 20
- vol% carbon dioxide, and reducing the pressure of the column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and
- (6) rinsing the column and adsorbent bed by feeding a mixture of hydrogen and nitrogen through the column
- 25
- and adsorbent bed
- the column and bed being at a pressure in the range of 1 to 5 bar a, and
- (7) pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably
- 30
- 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen.

One advantage of the present invention is that the method is suitable to obtain a pure carbon monoxide

stream from Fischer-Tropsch off-gas in step (3). This pure carbon monoxide stream can be recycled to the Fischer-Tropsch reactor. This makes it possible to convert most of the carbon atoms of the hydrocarbonaceous feed stock to the desired C₅+ hydrocarbons.

Another advantage of the present invention is from the Fischer-Tropsch off-gas a pure methane stream can be obtained in step (4).

The invention is further illustrated in the accompanying drawing.

Drawings

Figure 1A shows an overview of the process steps of a method according to the invention. Figure 1B shows an overview of the process steps of a preferred embodiment of the method of the present invention.

Figures 2 to 7 show parts of Fischer-Tropsch process line-ups each including an indication of the place in the process line-up at which the present invention may be applied.

Detailed Description of the Invention

The present invention relates to processing of off-gas obtained from a Fischer-Tropsch reactor in order to convert most of the carbon atoms of the hydrocarbonaceous feed stock to the desired C₅+ hydrocarbons. When removed from a Fischer-Tropsch reactor, the Fischer-Tropsch off-gas is generally at a temperature in the range of 40-100°C, preferably in the range of 50-70°C and at a pressure of 40-80 bar, preferably in the range of 50-70 bar.

Fischer-Tropsch off-gas is typically produced by a Fischer-Tropsch hydrocarbon synthesis process comprising the steps of:

- i) conversion of a (gaseous) hydrocarbonaceous feed to obtain synthesis gas (syngas);
- ii) catalytic conversion of the synthesis gas obtained in step i) using a Fischer-Tropsch catalyst into a Fischer-Tropsch product; and
- iii) separating the Fischer-Tropsch product of step ii) into at least one hydrocarbon product stream and a Fischer-Tropsch off-gas.

Suitably, syngas production methods include steam reforming of natural gas or liquid hydrocarbons and gasification of coal. Methods to convert (gaseous) hydrocarbonaceous feed into syngas include adiabatic oxidative reforming, autothermal reforming and partial oxidation. Preferably, hydrocarbonaceous feed is converted to syngas by partial oxidation at elevated temperature and pressure using an oxygen containing gas. Partial oxidation can take place according to various established processes. Catalytic as well as non-catalytic processes may be used. These processes include the Shell Gasification Process. A comprehensive survey of this process can be found in the Oil and Gas Journal, September 6, 1971, pp 86-90.

The H_2/CO ratio of the syngas is suitably between 1.5 and 2.3, preferably between 1.8 and 2.1. The catalysts used for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide into hydrocarbons are known in the art and are usually referred to as Fischer-Tropsch catalysts. Preferably, the catalysts for use in the Fischer-Tropsch hydrocarbon synthesis process comprises as the catalytically active component cobalt. The catalytically active component is preferably supported on a porous carrier, e.g. silica or titania. If desired, the Fischer-Tropsch catalyst may

also comprise one or more metals or metal oxides as promoters. Typically, the catalytic conversion may be effected at a temperature in the range of 150 to 350 °C, preferably from 180 to 270 °C. Typical total pressures for the catalytic conversion process are in the range of
5 from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute.

Generally, the Fischer-Tropsch hydrocarbon product stream is separated from the Fischer-Tropsch off-gas by a
10 gas/liquid separator.

The Fischer-Tropsch off-gas may comprise gaseous hydrocarbons, nitrogen, unconverted methane, unconverted carbon monoxide, carbon dioxide, hydrogen and water. The gaseous hydrocarbons are suitably C₁-C₅ hydrocarbons,
15 preferably C₁-C₄ hydrocarbons, more preferably C₁-C₃ hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethylether, may be present.

In most cases the Fischer-Tropsch off-gas will contain
20 10-40 wt% hydrogen, preferably 15-35 vol% hydrogen, 20-65 vol% CO, preferably 30-55 vol% CO, 10-50 vol% CO₂, especially 15-45 vol% CO₂, and 10-55 vol% N₂, especially 15-50 vol% N₂, calculated on the total volume of the gas
25 mixture. Depending on the syngas feed and the Fischer-Tropsch conditions the composition of the Fischer-Tropsch off-gas can vary. Obviously, the total volume of the gas mixture is 100 vol%.

The present invention provides a method for producing a
30 gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of the gas, from a gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen,

calculated on the total volume of the gas mixture, said method comprising, in sequence, the following steps:

- 5 (1) feeding a gas mixture through a column comprising an adsorbent bed, said gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture,
- 10 - with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure hydrogen, or with a mixture of hydrogen and nitrogen, and
- discharging effluent from the other end of said bed, and
- 15 - continuing said feeding and said discharging until a carbon monoxide comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated from the end of the bed at which the gas mixture is
- 20 being fed; and
- (2) ceasing the feeding of the gas mixture comprising methane, carbon dioxide, carbon monoxide and hydrogen, and reducing the pressure in the column and the bed with about 5 to 10 bar a; and
- 25 (3) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon dioxide, through the column and adsorbent bed,
- the column and bed being at a pressure in the range
- 30 of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
- discharging effluent from the other end of said bed, and

- continuing said feeding and said discharging until at least 60% of the carbon monoxide that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- 5 (4) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% carbon dioxide through the column and adsorbent bed,
- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more
- 10 preferably 30 to 55 bar a, and
- discharging effluent from the other end of said bed, and
- continuing said feeding and said discharging until at least 60% of the methane that was present in the
- 15 bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- (5) ceasing the feeding of a gas comprising at least 95 vol% carbon dioxide, and reducing the pressure of the column and adsorbent bed to a pressure in the range
- 20 of 1 to 5 bar a; and
- (6) rinsing the column and adsorbent bed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed
- the column and bed being at a pressure in the range
- 25 of 1 to 5 bar a, and
- (7) pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen.
- 30 In a preferred embodiment of the present invention repeated cycles of steps (1) to (7) are performed. Effluent from one step can be used as feeding gas in another step; this

is especially advantageous when repeated cycles of steps (1) to (7) are performed.

The method may be performed using a single column comprising an adsorbent bed. Preferably several columns that comprise an adsorbent bed are used. When using more than one column, the columns are preferably connected in parallel. Preferably the repeated cycles of steps (1) to (7) are performed over each column. In a preferred embodiment at least one column is subjected to one step of the cycle while another column is subjected to another step of the cycle. The product of one column can be used in another column, for example for purge, pressurization or rinse. In one embodiment at least two columns comprising an adsorbent bed, preferably at least seven columns comprising an adsorbent bed, are subjected to repeated cycles of steps (1) to (7). Preferably at most 21, more preferably at most 16, columns comprising an adsorbent bed are subjected to repeated cycles of steps (1) to (7).

The gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, preferably is a gaseous product from a Fischer-Tropsch reaction. In that case it may be referred to as Fischer-Tropsch off-gas. Fischer-Tropsch off-gas is typically produced by a Fischer-Tropsch hydrocarbon synthesis process comprising the steps of:

- i) conversion of a (gaseous) hydrocarbonaceous feed to obtain synthesis gas (syngas);
- ii) catalytic conversion of the synthesis gas obtained in step i) using a Fischer-Tropsch catalyst into a Fischer-Tropsch product; and

iii) separating the Fischer-Tropsch product of step ii) into at least one hydrocarbon product stream and a Fischer-Tropsch off-gas.

The off-gas obtained in step iii) may comprise gaseous hydrocarbons, nitrogen, unconverted methane, unconverted carbon monoxide, carbon dioxide, hydrogen and water. The gaseous hydrocarbons are suitably C₁-C₅ hydrocarbons, preferably C₁-C₄ hydrocarbons, more preferably C₁-C₃ hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethylether, may be present.

The gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, preferably comprises less than 10 volume %, more preferably less than 5 volume %, of hydrocarbons having 6 or more carbon atoms. More preferably the gas mixture comprises less than 10 volume %, more preferably less than 5 volume %, of hydrocarbons having 5 or more carbon atoms. Even more preferably the gas mixture comprises less than 10 volume %, more preferably less than 5 volume %, of hydrocarbons having 4 or more carbon atoms. In one embodiment hydrocarbons having 3 or more carbon atoms are removed from a Fischer-Tropsch off-gas, for example using a scrubber, before it is subjected to the method of the present invention. The gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, may comprise ethane. In a preferred embodiment the amount of ethane is less than 5 wt%, more preferably less than 2

wt%, and even more preferably less than 1 wt%, calculated on the total weight of the gas mixture.

The column comprising an adsorbent bed may be made of metal, preferably stainless steel. The adsorbent bed
5 may comprise, for example, alumina, a carbon molecular sieve, silicalite, activated carbon, a zeolite, or mixtures thereof. Preferably the adsorbent bed comprises activated carbon and/or zeolite. In another preferred
10 embodiment the adsorbent bed comprises activated carbon and/or silicalite. When alumina is used, it is preferably combined with a carbon molecular sieve, activated carbon silicalite and/or zeolite. If zeolite is used, it may for example be ZSM-5A and/or ZSM-13 X. If silicalite is used, preferably a silicalite with a high silica to alumina
15 molar ratio (SAR) is used. Activated carbon, silicalite and zeolite hardly adsorb nitrogen and hydrogen, but do adsorb carbon monoxide, methane, and carbon dioxide. Activated carbon, silicalite and zeolite are preferential adsorbers for methane and carbon dioxide as compared to
20 carbon monoxide.

The adsorbent bed and column are already pre-saturated and pre-pressurized with hydrogen or with a mixture of hydrogen and nitrogen upon commencement of feeding the gas mixture comprising methane, carbon
25 dioxide, carbon monoxide and hydrogen in step (1). The bed and column may be saturated and pressurized with pure hydrogen. Pure hydrogen comprises more than 90 volume %, preferably more than 95 vol %, and more preferably more than 99 vol % of hydrogen. The bed and column may be
30 saturated and pressurized with a mixture of hydrogen and nitrogen. The mixture of hydrogen and nitrogen preferably comprises hydrogen in a range of between 60 to 95 vol %, and nitrogen in a range of between 5 to 40 vol %. The

mixture of hydrogen and nitrogen preferably comprises less than 10 vol %, more preferably less than 5 vol %, even more preferably less than 1 vol % of gasses other than hydrogen and nitrogen. For example, the bed and
5 column may be saturated and pressurized with a product hydrogen and nitrogen comprising gas from step (1) of an earlier cycle.

In step (1), effluent is discharged from the other end of the adsorbent bed. The adsorbent bed will adsorb
10 methane, carbon dioxide and carbon monoxide. The effluent will mainly comprise hydrogen and nitrogen. A part of this effluent can be used to pressurize a column and adsorbent bed at the start of a cycle or in step (7). Another part of this effluent can be used in rinsing step
15 (6). Another part can be sent as feed to a Fischer-Tropsch reaction, even though it comprises nitrogen. The pressure of the effluent gas will be about the same as the pressure in the column and the adsorbent bed and will thus be in the range of 20 to 80 bar absolute (bar a),
20 preferably 30 to 70 bar a.

In step (1), the feeding of the gas mixture and the discharging of the effluent are continued until a carbon monoxide comprising gas has reached at least 45% of the length of the bed, preferably at least 50%, more
25 preferably at least 60%, and has reached at most 80% of the length of the bed, preferably at most 70%, calculated from the end of the bed at which the gas mixture is being fed. In a preferred embodiment, the feeding and discharging is ceased when the adsorption capacity of the
30 adsorbent bed towards carbon monoxide is reduced by 50% to 80%, preferably 60% to 70% from its adsorption capacity towards carbon monoxide when commencing the feeding of the gas mixture.

The progress of a carbon monoxide comprising gas through the bed can be monitored. This may, for example, be performed by analyzing gas samples of the effluent and/or gas samples from the column and adsorbent bed. The
5 progress of a carbon monoxide comprising gas through the bed may additionally or alternatively be monitored by determining the temperature along the length of the bed, e.g. by using thermocouples placed along the length of the bed. At the front of the carbon monoxide comprising
10 gas the temperature is increased as compared to the part of the bed that has not yet been reached by the carbon monoxide comprising gas. At the front of the carbon monoxide comprising gas the temperature is also increased as compared to the part of the bed where the carbon
15 monoxide has already been adsorbed in the adsorbent bed.

In step (2), ceasing the feeding of the gas mixture is performed by stopping the flow of gas to the column comprising an adsorbent bed. When the feeding and discharging is stopped, some hydrogen and nitrogen will
20 remain in the column containing an adsorbent bed. Upon ceasing the feeding of the gas mixture, the pressure in the column and adsorbent bed is reduced with about 5 to 10 bar a. The pressure reduction in the column and adsorbent bed suffices to let most of the effluent, which
25 comprises hydrogen and nitrogen, leave. The effluent leaves the column and bed at the same end from which effluent was discharged in step (1).

In step (3), a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon
30 dioxide, is fed to the column comprising an adsorbent bed. In step (3) preferably a gas comprising at least 99 vol% methane, or a gas comprising at least 99 vol% carbon dioxide, is fed to the column comprising an adsorbent

bed. In step (3), the gas is fed to the same end of the bed at which a gas mixture was fed in step (1).

The gas comprising at least 95 vol% methane, preferably at least 99 vol% methane, may, for example, be pure methane or treated natural gas. Treated natural gas is natural gas from which contaminants like water and sulfur have been removed. The gas comprising at least 95 vol% methane, preferably at least 99 vol% methane, may, for example, have the same composition as the hydrocarbonaceous feed that is converted into syngas for the Fischer-Tropsch reaction.

The gas comprising at least 95 vol% carbon dioxide, preferably at least 99 vol% carbon dioxide, may be or may comprise the effluent of step (5). Hence, the bed and column may be fed with a product carbon dioxide comprising gas from step (5) of an earlier cycle. In that case the product carbon dioxide comprising gas from step (5) of an earlier cycle is pressurized before it is used as feeding gas in step (3).

In step (3), effluent is discharged from the other end of the adsorbent bed. The adsorbent bed will adsorb even more methane in case methane is fed. The adsorbent bed will adsorb even more carbon dioxide in case carbon dioxide is fed. The effluent will mainly comprise carbon monoxide. Preferably the effluent comprises at least 80 vol%, more preferably at least 90 vol%, even more preferably at least 95 vol%, still more preferably at least 99 vol% carbon monoxide, calculated on the total volume of the effluent. The pressure of the effluent gas will be about the same as the pressure in the column and the adsorbent bed and will thus be in the range of 15 to 75 bar absolute (bar a), preferably 25 to 65 bar a, more preferably 30 to 55 bar a. The carbon monoxide product

stream can be used as feed for a Fischer-Tropsch reaction. It can, for example, be a recycle stream in a Fischer-Tropsch process. This is very advantageous as it makes it possible to convert most of the carbon atoms of the hydrocarbonaceous feed stock to the desired C₅+ hydrocarbons.

5

In one embodiment of the method of the present invention, an optionally scrubbed Fischer-Tropsch off-gas is used in step (1), and at least a part of the effluent of step (3) is sent as a recycle stream to the Fischer-Tropsch reactor that produced the off-gas.

10

In another embodiment, an optionally scrubbed Fischer-Tropsch off-gas from a first Fischer-Tropsch reactor is used in step (1), and at least a part of the effluent of step (3) is sent as a feed stream to a second Fischer-Tropsch reactor.

15

In a further embodiment at least a part of the effluent of step (3) is sent as a recycle stream to the Fischer-Tropsch reactor that produced the off-gas, and at least a part of the effluent of step (3) is sent as a feed stream to a second Fischer-Tropsch reactor.

20

In step (3), the feeding of methane, or of carbon dioxide, and the discharging of the effluent are continued until at least 60%, preferably at least 70%, more preferably at least 80%, even more preferably at least 90%, still more preferably at least 95% of the carbon monoxide that was present in the adsorbent bed at the commencement of this rinsing step is discharged from the other end of the bed. The methane, or the carbon dioxide, in the feed will replace carbon monoxide in the adsorbent bed. In a one embodiment, methane is fed in step (3) and the feeding and discharging is ceased when a breakthrough of methane is imminent. In this embodiment,

30

methane is thus fed until the adsorption capacity of the adsorbent bed towards methane is nil or almost nothing. In another embodiment, carbon dioxide is fed in step (3) and the feeding and discharging is ceased when a
5 breakthrough of methane is imminent.

The progress of a methane comprising gas through the bed can be monitored, e.g. by analyzing gas samples of the effluent and/or gas samples from the column and adsorbent bed. The progress of a methane comprising gas
10 through the bed may additionally or alternatively be monitored by determining the temperature along the length of the bed, e.g. by using thermocouples placed along the length of the bed. At the front of the methane comprising gas the temperature is increased as compared to the part
15 of the bed that has not yet been reached by the methane comprising gas. At the front of the methane comprising gas the temperature is also increased as compared to the part of the bed where the methane has already replaced carbon monoxide in the adsorbent bed, or where the carbon
20 dioxide has replaced the carbon monoxide and subsequently the methane in the adsorbent bed.

In step (4), a gas comprising at least 95 vol% carbon dioxide is fed to the column comprising an adsorbent bed. In step (4) preferably a gas comprising at
25 least 99 vol% carbon dioxide is fed to the column comprising an adsorbent bed. In step (4), the gas is fed to the same end of the bed at which a gas mixture was fed in step (1).

The gas comprising at least 95 vol% carbon dioxide, preferably at least 99 vol% dioxide, may be or may
30 comprise the effluent of step (5). Hence, the bed and column may be fed with a product carbon dioxide comprising gas from step (5) of an earlier cycle. In that

case the product carbon dioxide comprising gas from step (5) of an earlier cycle is pressurized before it is used as feeding gas in step (4).

5 In step (4), effluent is discharged from the other end of the adsorbent bed. The adsorbent bed will adsorb even more carbon dioxide. The effluent will mainly comprise methane. The pressure of the effluent gas will be about the same as the pressure in the column and the adsorbent bed and will thus be in the range of 15 to 75
10 bar absolute (bar a), preferably 25 to 65 bar a, more preferably 30 to 55 bar a. A methane product stream is obtained. The methane product stream preferably comprises at least 80 vol% methane, more preferably at least 90 vol% methane, even more preferably at least 95% methane.

15 In step (4), the feeding of carbon dioxide and the discharging of the effluent are continued until at least 60%, preferably at least 70%, more preferably at least 80%, even more preferably at least 90%, still more preferably at least 95% of the methane that was present
20 in the adsorbent bed at the commencement of this rinsing step is discharged from the other end of the bed. The carbon dioxide in the feed will replace methane in the adsorbent bed. In a preferred embodiment, the feeding and discharging is ceased when the adsorption capacity of the
25 adsorbent bed towards carbon dioxide is nil or almost nothing.

The progress of a carbon dioxide comprising gas through the bed can be monitored, e.g. by analyzing gas samples of the effluent and/or gas samples from the
30 column and adsorbent bed. The progress of a carbon dioxide comprising gas through the bed may additionally or alternatively be monitored by determining the temperature along the length of the bed, e.g. by using

thermocouples placed along the length of the bed. At the front of the carbon dioxide comprising gas the temperature is increased as compared to the part of the bed that has not yet been reached by the carbon dioxide comprising gas. At the front of the carbon dioxide comprising gas the temperature is also increased as compared to the part of the bed where the carbon dioxide has already replaced methane in the adsorbent bed.

In step (5), the feeding of a gas comprising at least 95 vol% carbon dioxide is ceased. The pressure of the column and adsorbent bed is reduced to a pressure in the range of 1 to 5 bar a. During step (5) carbon dioxide leaves the column and bed at the same end at which in step (4) carbon dioxide was fed to the column and bed. A part of this effluent can be pressurized and then used in step (3) and/or step (4) of a next cycle. Another part of this effluent can be sent to a fuel pool, to a gasifier, or to a steam methane reformer (SMR). During step (5) almost all carbon monoxide leaves the column and bed.

In step (6), the column and adsorbent bed are rinsed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed. The mixture of hydrogen and nitrogen is fed to the same end of the column and bed from which effluent was discharged in step (1). During step (6) residual carbon dioxide leaves the column and bed at the same end at which in step (1) a gas mixture was fed to the column and bed. In a preferred embodiment, the mixture of hydrogen and nitrogen used in step (6) is a part of the effluent from step (2), and may optionally also comprise a part of the effluent from step (1). The gas mixture fed to the column and bed rinses the bed from carbon dioxide. The pressure of the effluent gas will be about the same as the pressure in the column and the

adsorbent bed and will thus be in the range of 1 to 5 bar a. The effluent can be sent to a fuel pool.

In a preferred embodiment, the column and adsorbent bed are rinsed in step (6) by feeding a gas comprising at least 95 vol% nitrogen, preferably at least 99 vol% nitrogen, through the column and adsorbent bed, followed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed, whereby the column and bed are at a pressure in the range of 1 to 5 bar a. The gas comprising at least 95 vol% nitrogen, preferably at least 99 vol% nitrogen, may be the product of an air separation unit (ASU). The mixture of hydrogen and nitrogen preferably is a part of the effluent from step (2), and may optionally also comprise a part of the effluent from step (1). The gas comprising at least 95 vol% nitrogen, and in a subsequent step the mixture of hydrogen and nitrogen, are fed to the same end of the column and bed from which effluent was discharged in step (1). When the gas comprising at least 95 vol% nitrogen is fed to the column and bed, a part of the residual carbon dioxide leaves the column and bed at the same end at which in step (1) a gas mixture was fed to the column and bed. This effluent can be sent to a fuel pool. When in a subsequent step the mixture of hydrogen and nitrogen is fed to the column and bed, further residual carbon dioxide leaves the column and bed at the same end at which in step (1) a gas mixture was fed to the column and bed. This effluent can be sent to a fuel pool.

In step (7) the column and adsorbent bed are pressurized to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen. The mixture used may comprise a part of the product hydrogen

and nitrogen from step (2), and may optionally also comprise a part of the product hydrogen and nitrogen from step (1). The mixture of hydrogen and nitrogen preferably comprises hydrogen in a range of between 60 to 95 vol %, and nitrogen in a range of between 5 to 40 vol %. The mixture of hydrogen and nitrogen preferably comprises less than 10 vol %, more preferably less than 5 vol %, even more preferably less than 1 vol % of gases other than hydrogen and nitrogen.

In a preferred embodiment, the invention provides a method for producing a gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of the gas, from a gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, said method comprising, in sequence, the following steps:

- (1) feeding a gas mixture through a column comprising an adsorbent bed, said gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture,
 - with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure hydrogen, or with a mixture of hydrogen and nitrogen, and
 - discharging effluent from the other end of said bed, and
 - continuing said feeding and said discharging until a carbon monoxide comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated

from the end of the bed at which the gas mixture is being fed; and

(2) ceasing the feeding of the gas mixture comprising methane, carbon dioxide, carbon monoxide and hydrogen, and reducing the pressure in the column and the bed with about 5 to 10 bar a; and

(3) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon dioxide, through the column and adsorbent bed,

- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and

- discharging effluent from the other end of said bed, and

- continuing said feeding and said discharging until at least 60% of the carbon monoxide that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and

(4) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% carbon dioxide through the column and adsorbent bed,

- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and

- discharging effluent from the other end of said bed, and

- continuing said feeding and said discharging until at least 60% of the methane that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and

(5) ceasing the feeding of a gas comprising at least 95 vol% carbon dioxide, and reducing the pressure of the

column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and

(6) rinsing the column and adsorbent bed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed

- the column and bed being at a pressure in the range of 1 to 5 bar a, and

(7) pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen,

said method further comprising, in sequence, the following steps:

(A) feeding the effluent of step (1) through a column comprising an adsorbent bed,

- with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure

hydrogen and

- discharging effluent from the other end of said bed, and

- continuing said feeding and said discharging until a nitrogen comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated from the end of the bed at which the gas mixture is being fed; and

(B) ceasing the feeding of the effluent of step (1), and reducing the pressure in the column and the bed with about 2 to 5 bar a; and

(C) further reducing the pressure in the column and the bed with about 2 to 5 bar a; and

- (D) reducing the pressure of the column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and
- (E) rinsing the column and adsorbent bed by feeding pure hydrogen through the column and adsorbent bed
- 5 - the column and bed being at a pressure in the range of 1 to 5 bar a, and
- (F) pressurizing the column and adsorbent bed to a pressure in the range of 5 to 50 bar a, preferably 10 to 45 bar a, more preferably 20 to 40 bar a by
- 10 feeding hydrogen, and
- (G) further pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding hydrogen.

15 In this preferred embodiment, besides a gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of this carbon monoxide comprising gas, preferably also a gas comprising at least 80 vol% hydrogen, calculated on the total volume of this hydrogen comprising gas, is produced. The gas

20 comprising at least 80 vol % carbon monoxide is effluent from step (3). The gas preferably comprising at least 80 vol % hydrogen is obtained in steps (A), (B), (C), (F) and (G).

One advantage of the present invention is that the method is suitable to obtain a pure carbon monoxide

25 stream from Fischer-Tropsch off-gas in step (3). This pure carbon monoxide stream can be recycled to the Fischer-Tropsch reactor. This makes it possible to convert most of the carbon atoms of the hydrocarbonaceous feed stock to the desired C₅+ hydrocarbons.

30 A further advantage is that the method is suitable to obtain a pure methane stream from Fischer-Tropsch off-gas in step (4).

Another advantage of the present invention is that the method is suitable to obtain a pure hydrogen stream from Fischer-Tropsch off-gas in step (A). This pure hydrogen stream can be recycled to the Fischer-Tropsch reactor and/or it can be used in another process that requires hydrogen, for example when adjusting the H₂/CO ratio of a feed to a second Fischer-Tropsch reactor.

As the process of the present invention allows a recycle of both carbon monoxide and hydrogen from a Fischer-Tropsch off-gas, it is a suitable method for recycling unconverted syngas.

As described above, steps (1) to (7) may be performed using a single column comprising an adsorbent bed. As described above, preferably repeated cycles of steps (1) to (7) are performed.

In a preferred embodiment of the present invention repeated cycles of steps (A) to (G) are performed. Effluent from one step can be used as feeding gas in another step; this is especially advantageous when repeated cycles of steps (A) to (G) are performed.

Steps (A) to (G) may be performed using a single column comprising an adsorbent bed. Preferably several columns that comprise an adsorbent bed are used. When using more than one column, the columns are preferably connected in parallel. Preferably the repeated cycles of steps (A) to (G) are performed over each column. In a preferred embodiment at least one column is subjected to one step of the cycle while another column is subjected to another step of the cycle. The product of one column can be used in another column, for example for purge, pressurization or rinse. In one embodiment at least two columns comprising an adsorbent bed, preferably at least five columns comprising an adsorbent bed, are subjected

to repeated cycles of steps (A) to (G). Preferably at most 20, more preferably at most 15, columns comprising an adsorbent bed are subjected to repeated cycles of steps (A) to (G).

5 The feed gas for step (A) is at least a part of the effluent of step (1).

 The feed gas for step (A) preferably comprises 10 to 40 volume% nitrogen and 60 to 90 volume% hydrogen. More preferably the feed gas for step (A) comprises 15 to 35
10 volume% nitrogen and 65 to 85 volume% hydrogen.

 The column comprising an adsorbent bed may be made of metal, preferably stainless steel. The adsorbent bed may comprise, for example, alumina, a carbon molecular sieve, silicalite, activated carbon, a zeolite, or
15 mixtures thereof. Preferably the adsorbent bed comprises a zeolite. When alumina is used, it is combined with a zeolite. The zeolite may for example be ZSM-5A and/or ZSM-13 X and/or a LiX zeolite. Zeolite is a preferential adsorber for nitrogen as compared to hydrogen.

20 The adsorbent bed and column are already pre-saturated and pre-pressurized with hydrogen upon commencement of feeding the effluent of step (1) in step (A). The bed and column may be saturated and pressurized with pure hydrogen. Pure hydrogen comprises more than 90
25 volume %, preferably more than 95 vol %, and more preferably more than 99 vol % of hydrogen. The bed and column may be saturated and pressurized with a product hydrogen comprising gas from step (A) of an earlier cycle.

30 In step (A), effluent is discharged from the other end of the adsorbent bed. The adsorbent bed will adsorb nitrogen. The effluent will mainly comprise hydrogen. A part of this effluent can be used to pressurize a column

and adsorbent bed at the start of a cycle or in step (G). Another part can be sent as feed to a Fischer-Tropsch reaction. The pressure of the effluent gas will be about the same as the pressure in the column and the adsorbent bed and will thus be in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a.

In step (A), the feeding of the gas mixture and the discharging of the effluent are continued until a front of nitrogen comprising gas has reached at least 45% of the length of the bed, preferably at least 50%, more preferably at least 60%, and has reached at most 80% of the length of the bed, preferably at most 70%, calculated from the end of the bed at which the gas mixture is being fed. In a preferred embodiment, the feeding and discharging is ceased when the adsorption capacity of the adsorbent bed towards nitrogen is reduced by 50% to 80%, preferably 60% to 70% from its adsorption capacity towards nitrogen when commencing the feeding of the gas mixture. The progress of a nitrogen comprising gas through the bed can be monitored, e.g. by analyzing gas samples of the effluent and/or gas samples from the column and adsorbent bed. The progress of a nitrogen comprising gas through the bed may additionally or alternatively be monitored by determining the temperature along the length of the bed, e.g. by using thermocouples placed along the length of the bed. At the front of the nitrogen comprising gas the temperature is increased as compared to the part of the bed that has not yet been reached by the nitrogen comprising gas. At the front of the nitrogen comprising gas the temperature is also increased as compared to the part of the bed where nitrogen has already been adsorbed.

In step (B), ceasing the feeding of the gas mixture is performed by stopping the flow of gas to the column comprising an adsorbent bed. When the feeding and discharging is stopped, some hydrogen and nitrogen will remain in the column containing an adsorbent bed. Upon ceasing the feeding of the gas mixture, the pressure in the column and adsorbent bed is preferably reduced with in total about 5 to 10 bar a in steps (B) and (C). Most preferably steps (B) and (C) are performed as separate steps. It is also possible to combine steps (B) and (C) and reduce the pressure in the column and adsorbent bed with in total about 5 to 10 bar a in a single step. When steps (B) and (C) are performed separately, the pressure in the column and bed is reduced in step (B) with about 2 to 5 bar a, and is further reduced in step (C) with another 2 to 5 bar a. The pressure reduction in the column and adsorbent bed suffices to let most of the effluent, which comprises hydrogen, leave. During steps (B) and (C) the effluent leaves the column and bed at the same end from which effluent was discharged in step (A).

In step (D), the pressure of the column and adsorbent bed is reduced to a pressure in the range of 1 to 5 bar a. During step (D) hydrogen and nitrogen leave the column and bed at the same end at which in step (A) effluent of step (1) was fed to the column and bed. The effluent can be sent to a fuel pool. During step (D) almost all hydrogen and nitrogen leave the column and bed.

In step (E), the column and adsorbent bed are rinsed by feeding hydrogen through the column and adsorbent bed. The hydrogen is fed to the same end of the column and bed from which effluent was discharged in step (A). During step (E) residual nitrogen leaves the column and bed at

the same end at which in step (A) an effluent from step (1) was fed to the column and bed. In a preferred embodiment, the hydrogen used in step (E) is a part of the effluent from step (C), and may optionally also
5 comprise a part of the effluent from step (B) and/or (A). The hydrogen fed to the column and bed rinses the bed from nitrogen. The pressure of the effluent gas will be about the same as the pressure in the column and the adsorbent bed and will thus be in the range of 1 to 5 bar
10 a. The effluent can be sent to a fuel pool. Additionally or alternatively at least a part of the effluent of step (E) can be used as a feeding gas in step (6).

In steps (F) and (G) the column and adsorbent bed are pressurized to a pressure in the range of 15 to 75
15 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding hydrogen. In step (F), the hydrogen used may be or may comprise a part of the product hydrogen from step (B), and may optionally also comprise a part of the product hydrogen from step (A). In step
20 (G), the hydrogen preferably is a part of the product hydrogen from step (A). Most preferably steps (F) and (G) are performed as separate steps. When steps (F) and (G) are performed separately, the column and bed are pressurized in step (F) to a pressure in the range of 5
25 to 50 bar a, preferably 10 to 45 bar a, more preferably 20 to 40 bar a, and is further pressurized in step (G) to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a. It is also possible to combine steps (F) and (G) and pressurize the
30 column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding hydrogen in a single step using

hydrogen from step (A) and optionally also hydrogen from step (B).

In a another preferred embodiment, the invention provides a method for producing a gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of the gas, from a gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, said method comprising, in sequence, the following steps:

- (1) feeding a gas mixture through a column comprising an adsorbent bed, said gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture,
 - with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure hydrogen, or with a mixture of hydrogen and nitrogen, and
 - discharging effluent from the other end of said bed, and
 - continuing said feeding and said discharging until a carbon monoxide comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated from the end of the bed at which the gas mixture is being fed; and
- (2) ceasing the feeding of the gas mixture comprising methane, carbon dioxide, carbon monoxide and hydrogen, and reducing the pressure in the column and the bed with about 5 to 10 bar a; and

- (3) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon dioxide, through the column and adsorbent bed,
- 5 - the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
- discharging effluent from the other end of said bed, and
- 10 - continuing said feeding and said discharging until at least 60% of the carbon monoxide that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- (4) rinsing the column and the adsorbent bed by feeding a gas
- 15 comprising at least 95 vol% carbon dioxide through the column and adsorbent bed,
- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
- 20 - discharging effluent from the other end of said bed, and
- continuing said feeding and said discharging until at least 60% of the methane that was present in the bed at the commencement of this rinsing step is
- 25 discharged from the other end of said bed; and
- (5) ceasing the feeding of a gas comprising at least 95 vol% carbon dioxide, and reducing the pressure of the column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and
- 30 (6) rinsing the column and adsorbent bed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed

- the column and bed being at a pressure in the range of 1 to 5 bar a, and

(7) pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen, said method further comprising, in sequence, the following steps:

- (I) sending at least a part of the discharged effluent of step (1) as feed to a membrane unit,
- (II) optionally sending at least a part of the discharged effluent of step (3) as sweep gas to the membrane unit,
- (III) optionally sending at least a part of the retentate of the membrane unit as feed to step (6),
- (IV) sending at least a part of the permeate of the membrane unit as feed to a Fischer-Tropsch reaction.

In this preferred embodiment of the present invention a gas stream comprising hydrogen and carbon monoxide is produced which may be used as feed for a Fischer-Tropsch reaction. The produced gas comprising at least 80% carbon monoxide, which is effluent of step (3), may be partly or completely used to produce the gas stream comprising hydrogen and carbon monoxide.

In a preferred embodiment steps (II) and (III) are performed.

Steps (I) to (IV) and steps (A) to (G) as described above preferably are not combined. The process of the present invention preferably has either additional steps (A) to (G) or additional steps (I) to (IV).

The membrane unit that can be used can comprise a polymeric membrane or a ceramic membrane, preferably a

polymeric membrane, most preferably a polyimide membrane. Such membranes are commercially available.

Discharged effluent of step (1) comprises nitrogen and hydrogen and is sent as feed to a membrane unit. Also
5 a sweep gas is sent to the membrane unit. The sweep gas preferably comprises carbon monoxide and may be discharged effluent of step (3).

In the membrane unit, feed comprising nitrogen and hydrogen is sent to one side of the membrane and sweep
10 gas comprising carbon monoxide is sent to the other side of the membrane. The feed comprising nitrogen and hydrogen which is sent as feed to one side of the membrane preferably is at a higher pressure as compared to the sweep gas comprising carbon monoxide which is sent
15 to the other side of the membrane. The feed may, for example, be at a pressure in the range of from 30 to 70 bar a.

In the membrane unit, hydrogen flows through the membrane. Preferably nitrogen and carbon monoxide do not
20 or hardly flow through the membrane. Hydrogen present in the feed to the membrane unit becomes part of the permeate. The permeate of the membrane unit comprises carbon monoxide and hydrogen. Permeate may be sent as feed to a Fischer-Tropsch reaction. The retentate of the
25 membrane unit comprises nitrogen. Retentate may be sent as feed to step (6).

Some embodiments of the method according to the invention will be illustrated below with reference to the
attached figures. It is noted that the present invention
30 should not be considered limited thereto or thereby.

Figure 1A illustrates an overview of the process steps of a method according to the invention. The column comprising an adsorbent bed is depicted seven times; each

time it shows a step of the method according to the invention. In step (1) Fischer-Tropsch off-gas is fed to the column and bed and a mixture of hydrogen and nitrogen is discharged. During step (1) the pressure in the column and bed is high. In step (2) the pressure is reduced by 5 to 10 bar a, and a remainder of hydrogen and nitrogen is discharged. In step (3) the column and bed are rinsed by feeding them with carbon dioxide and discharging carbon monoxide. The carbon monoxide stream can be sent as feed to a Fischer-Tropsch reaction. In step (4) the column and bed are further rinsed by feeding them with carbon dioxide and discharging methane. Methane is obtained as a product stream. In step (5) the pressure in the column and bed is reduced to 1 to 5 bar a, and carbon dioxide is discharged. In step (6) a mixture of hydrogen and nitrogen is fed to the column and bed and the effluent may be sent to the fuel pool. In step (7) the column and bed are pressurized to a high pressure again using a mixture of hydrogen and nitrogen.

Figure 1B shows an overview of the process steps of a preferred embodiment of the method of the present invention. One column comprising an adsorbent bed is depicted seven times; each time it shows a step of steps (1) to (7) according to the invention. Another column comprising an adsorbent bed is depicted seven times; each time it shows a step of steps (A) to (G) according to the invention. In step (1) Fischer-Tropsch off-gas is fed to the column and bed and a mixture of hydrogen and nitrogen is discharged. During step (1) the pressure in the column and bed is high. In step (2) the pressure is reduced by 5 to 10 bar a, and a remainder of hydrogen and nitrogen is discharged. In step (3) the column and bed are rinsed by feeding them with carbon dioxide and discharging carbon

monoxide. The carbon monoxide stream can be sent as feed to a Fischer-Tropsch reaction. In step (4) the column and bed are further rinsed by feeding them with carbon dioxide and discharging methane. Methane is obtained as a product stream. In step (5) the pressure in the column and bed is reduced to 1 to 5 bar a, and carbon dioxide is discharged. In step (6) a mixture of hydrogen and nitrogen is fed to the column and bed and the effluent may be sent to the fuel pool. In step (7) the column and bed are pressurized to a high pressure again using a mixture of hydrogen and nitrogen. In step (A) effluent from step (1) is fed to the column and bed and hydrogen is discharged. During step (A) the pressure in the column and bed is high. In steps (B) and (C) the pressure is reduced in total by 5 to 10 bar a, and a remainder of hydrogen is discharged. In step (D) the pressure in the column and bed is reduced to 1 to 5 bar a, and hydrogen and nitrogen are discharged. In step (E) hydrogen is fed to the column and bed and the effluent may be sent to the fuel pool. In steps (F) and (G) the column and bed are pressurized to a high pressure again using hydrogen.

Figures 2 to 7 illustrate overviews of parts of Fischer-Tropsch process line-ups each indicating a place at which the method according to the invention can be applied.

Figure 2 concerns a part of a process line-up comprising a single Fischer-Tropsch reactor HPS. The unit in which the method of the invention is performed is indicated with the word "Separator". In this line-up a scrubber is placed between the Fischer-Tropsch reactor HPS and the unit in which the method of the invention is performed (Separator) in order to remove hydrocarbons with 3 or more carbon atoms before the Fischer-Tropsch

off-gas is fed to step (1) of the method of the present invention. Product gas comprising CO from step (3) is recycled from the Separator to the Fischer-Tropsch reactor HPS.

5 Figure 3 concerns a part of a process line-up comprising a single Fischer-Tropsch reactor HPS. In this line-up a part of the scrubbed off-gas is sent to a steam methane reformer (SMR), and a part of the scrubbed off-gas is sent to the Separator, i.e. the unit for method
10 according to the invention. Product gas comprising CO from step (3) is recycled from the Separator to the Fischer-Tropsch reactor HPS. A part of the effluent from step (5) and the effluent of step (6) are sent to the fuel pool.

15 Figure 4 concerns a part of a process line-up comprising a single Fischer-Tropsch reactor HPS. In this line-up a part of the effluent from step (5) is recycled to the syngas production unit.

 Figure 5 concerns a part of a process line-up
20 comprising a first Fischer-Tropsch reactor HPS 1 (not shown) and a second Fischer-Tropsch reactor HPS 2. The unit in which the method of the invention is performed is indicated with the word "Separator". In this line-up a scrubber is placed between the second Fischer-Tropsch
25 reactor HPS 2 and the unit in which the method of the invention is performed (Separator) in order to remove hydrocarbons with 3 or more carbon atoms before the Fischer-Tropsch off-gas is fed to step (1) of the method of the present invention. Product gas comprising CO from
30 step (3) is recycled from the Separator to the Fischer-Tropsch reactor HPS 2.

 Figure 6 concerns a part of a process line-up comprising a first Fischer-Tropsch reactor HPS 1 and a

second Fischer-Tropsch reactor HPS 2. Scrubbed off-gas from Fischer-Tropsch reactor HPS 1 is sent to step (1) of the method according to the invention which takes place in the Separator. Product gas comprising CO from step (3) is sent as a feed stream to Fischer-Tropsch reactor HPS 2.

Figure 7 concerns a part of a process line-up comprising a first Fischer-Tropsch reactor HPS 1 (not shown) and a second Fischer-Tropsch reactor HPS 2. A part of the scrubbed off-gas is sent to an SMR and a part of the scrubbed off-gas is sent to the Separator, i.e. the unit for the process of the present invention. Product gas comprising CO from step (3) is recycled from the Separator to the Fischer-Tropsch reactor HPS 2.

While the method has been described in terms of what are presently considered to be the most practical and preferred embodiments, it is to be understood that the disclosure need not be limited to the disclosed embodiments. It is intended to cover various modifications, combinations and similar arrangements included within the spirit and scope of the claims, the scope of which should be accorded the broadest interpretation so as to encompass all such modifications and similar structures. The present disclosure includes any and all embodiments of the following claims.

It should also be understood that a variety of changes may be made without departing from the essence of the invention. Such changes are also implicitly included in the description. They still fall within the scope of this invention. It should be understood that this disclosure is intended to yield a patent covering numerous aspects of the invention both independently and

as an overall system and in both method and apparatus modes.

Any patents, publications, or other references mentioned in this application for patent are hereby
5 incorporated by reference. In addition, as to each term used, it should be understood that unless its utilization in this application is inconsistent with such interpretation, common dictionary definitions should be understood as incorporated for each term and all
10 definitions, alternative terms, and synonyms such as contained in at least one of a standard technical dictionary recognized by artisans.

C L A I M S

1. A method for producing a gas comprising at least 80 vol% carbon monoxide, calculated on the total volume of the gas, from a gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, said method comprising, in sequence, the following steps:

- (1) feeding a gas mixture through a column comprising an adsorbent bed, said gas mixture comprising 5-50 vol% methane, 10-50 vol% carbon dioxide, 20-65 vol% carbon monoxide, 10-40 wt% hydrogen and 10-55 vol% nitrogen, calculated on the total volume of the gas mixture, - with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure hydrogen, or with a mixture of hydrogen and nitrogen, and - discharging effluent from the other end of said bed, and - continuing said feeding and said discharging until a carbon monoxide comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated from the end of the bed at which the gas mixture is being fed; and
- (2) ceasing the feeding of the gas mixture comprising methane, carbon dioxide, carbon monoxide and hydrogen, and reducing the pressure in the column and the bed with about 5 to 10 bar a; and

- (3) rinsing the column and the adsorbent bed by feeding a gas comprising at least 95 vol% methane, or a gas comprising at least 95 vol% carbon dioxide, through the column and adsorbent bed,
- 5 - the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
- discharging effluent from the other end of said bed, and
- 10 - continuing said feeding and said discharging until at least 60% of the carbon monoxide that was present in the bed at the commencement of this rinsing step is discharged from the other end of said bed; and
- (4) rinsing the column and the adsorbent bed by feeding a gas
- 15 comprising at least 95 vol% carbon dioxide through the column and adsorbent bed,
- the column and bed being at a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a, and
- 20 - discharging effluent from the other end of said bed, and
- continuing said feeding and said discharging until at least 60% of the methane that was present in the bed at the commencement of this rinsing step is
- 25 discharged from the other end of said bed; and
- (5) ceasing the feeding of a gas comprising at least 95 vol% carbon dioxide, and reducing the pressure of the column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and
- 30 (6) rinsing the column and adsorbent bed by feeding a mixture of hydrogen and nitrogen through the column and adsorbent bed

- the column and bed being at a pressure in the range of 1 to 5 bar a, and

(7) pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding a mixture of hydrogen and nitrogen, whereby said method optionally further comprises, either in sequence, the following steps:

(A) feeding the effluent of step (1) through a column comprising an adsorbent bed,

- with upon commencement of said feeding, the bed and column being pre-saturated and pre-pressurized to a pressure in the range of 20 to 80 bar absolute (bar a), preferably 30 to 70 bar a, with pure

hydrogen and

- discharging effluent from the other end of said bed, and

- continuing said feeding and said discharging until a nitrogen comprising gas has reached at least 45% of the length of the bed and has reached at most 80% of the length of the bed, calculated from the end of the bed at which the gas mixture is being fed; and

(B) ceasing the feeding of the effluent of step (1), and reducing the pressure in the column and the bed with about 2 to 5 bar a; and

(C) further reducing the pressure in the column and the bed with about 2 to 5 bar a; and

(D) reducing the pressure of the column and adsorbent bed to a pressure in the range of 1 to 5 bar a; and

(E) rinsing the column and adsorbent bed by feeding pure hydrogen through the column and adsorbent bed

- the column and bed being at a pressure in the range of 1 to 5 bar a, and

(F) pressurizing the column and adsorbent bed to a pressure in the range of 5 to 50 bar a, preferably 10 to 45 bar a, more preferably 20 to 40 bar a by feeding hydrogen, and

5 (G) further pressurizing the column and adsorbent bed to a pressure in the range of 15 to 75 bar a, preferably 25 to 65 bar a, more preferably 30 to 55 bar a by feeding hydrogen,

or, in sequence, the following steps:

10 (I) sending at least a part of the discharged effluent of step (1) as feed to a membrane unit,

(II) optionally sending at least a part of the discharged effluent of step (3) as sweep gas to the membrane unit,

15 (III) optionally sending at least a part of the retentate of the membrane unit as feed to step (6),

(IV) sending at least a part of the permeate of the membrane unit as feed to a Fischer-Tropsch reaction.

20 2. A method according to claim 1, wherein repeated cycles of steps (1) to (7) are performed, or wherein repeated cycles of steps (1) to (7) are performed and repeated cycles of steps (A) to (G) are performed.

25

3. A method according to claim 1 or 2, wherein at least two, preferably at least seven, columns that comprise an adsorbent bed are used for steps (1) to (7),

or wherein steps (A) to (G) are performed and at least
30 two, preferably at least seven, columns that comprise an adsorbent bed are used for steps (1) to (7) and at least two, preferably at least five, columns that comprise an adsorbent bed are used for steps (A) to (G).

4. A method according to claim 3, wherein the columns
for steps (1) to (7) are connected in parallel,
or wherein steps (A) to (G) are performed and the columns
5 for steps (1) to (7) are connected in parallel, and the
columns for steps (A) to (G) are connected in parallel.

5. A method according to any one of the preceding
claims, wherein the gas mixture comprising methane,
10 carbon dioxide, carbon monoxide and hydrogen is Fischer-
Tropsch off-gas.

6. A method according to any one of the preceding
claims, wherein at least a part of the discharged
15 effluent of step (3) is sent as feed to a Fischer-Tropsch
reaction,
or wherein steps (A) to (G) are performed and at least a
part of the discharged effluent of step (3) is sent as
feed to a Fischer-Tropsch reaction, and at least a part
20 of the discharged effluent of step (A) is sent,
separately or in combination with effluent of step (3),
as a feed to a Fischer-Tropsch reaction.

7. A method according to any one of the preceding
25 claims, wherein the column and adsorbent bed are rinsed in
step (6)

- by feeding a gas comprising at least 95 vol% nitrogen,
preferably at least 99 vol% nitrogen, through the column
and adsorbent bed,

- followed by feeding a mixture of hydrogen and nitrogen
30 through the column and adsorbent bed,

- the column and bed being at a pressure in the range of
1 to 5 bar a.

8. A method according to any one of the preceding claims, wherein a part of the effluent of step (2) is used as feeding gas in step (6),
5 or wherein and steps (A) to (G) are performed and a part of the effluent of step (2) is used as feeding gas in step (6), and at least a part of the discharged effluent of step (E) is used, separately or in combination with effluent of step (2), as a feeding gas in step (6).

10

9. A method according to claim 8, wherein additionally a part of the effluent of step (1) is used as feeding gas in step (6).

15

10. A method according to any one of the preceding claims, wherein a part of the effluent of step (2) is used as feeding gas in step (7).

20

11. A method according to claim 10, wherein additionally a part of the effluent of step (1) is used as feeding gas in step (7).

25

12. A method according to any one of the preceding claims, wherein repeated cycles of steps (1) to (7) are performed and a part of the effluent of step (5) is pressurized and used as feeding gas in step (3) and/or step (4) of a next cycle.

30

13. A method according to any one of the preceding claims, wherein an optionally scrubbed Fischer-Tropsch off-gas from a Fischer-Tropsch reactor is fed to the column and adsorbent bed in step (1), and a part of the

effluent of step (3) is sent as a recycle stream to the Fischer-Tropsch reactor that produced the off-gas.

5 14. A method according to any one of the preceding claims, wherein an optionally scrubbed Fischer-Tropsch off-gas from a first Fischer-Tropsch reactor is used in step (1), and a part of the effluent of step (3) is sent as a feed stream to a second Fischer-Tropsch reactor.

FIG. 1 A

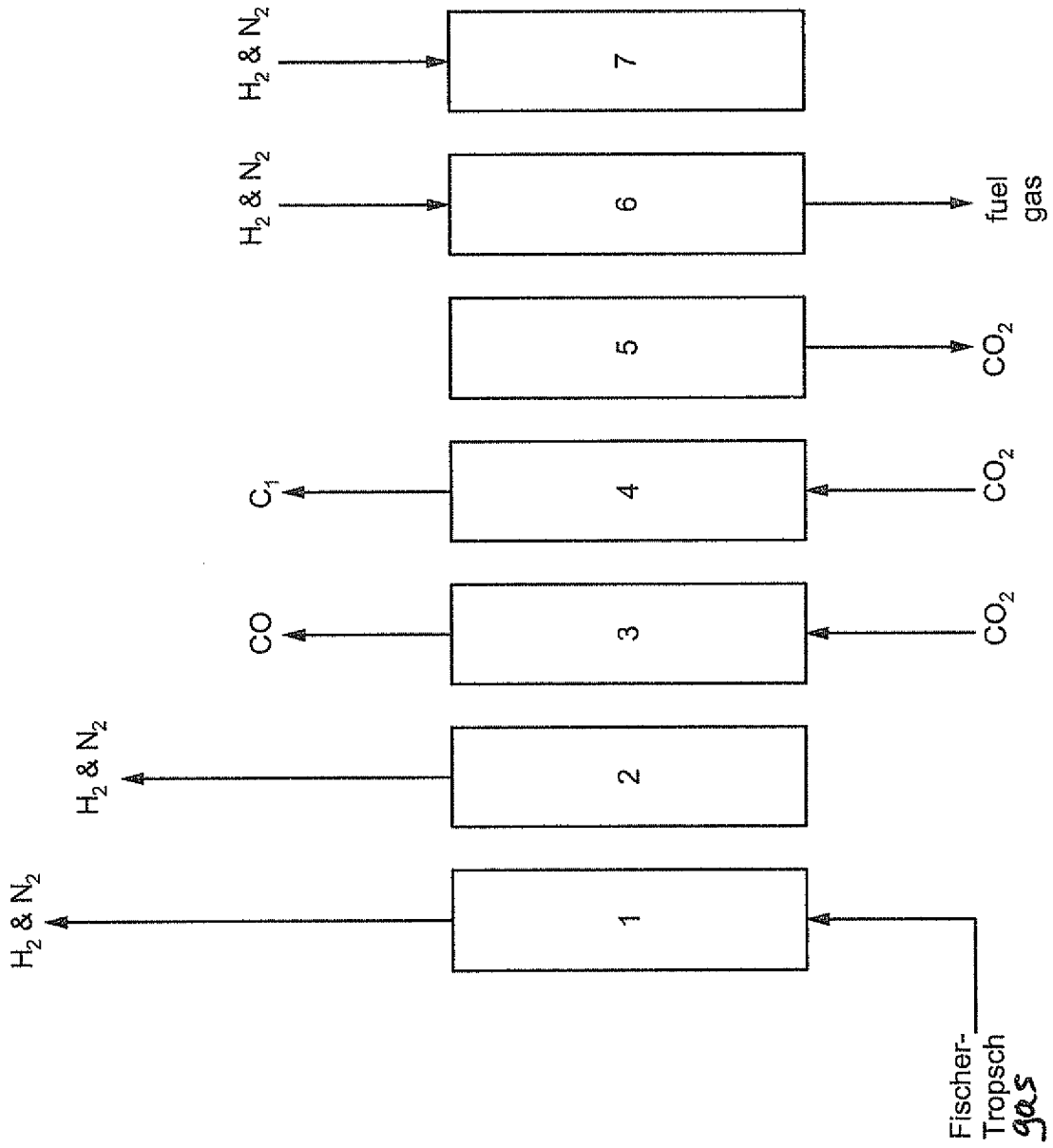
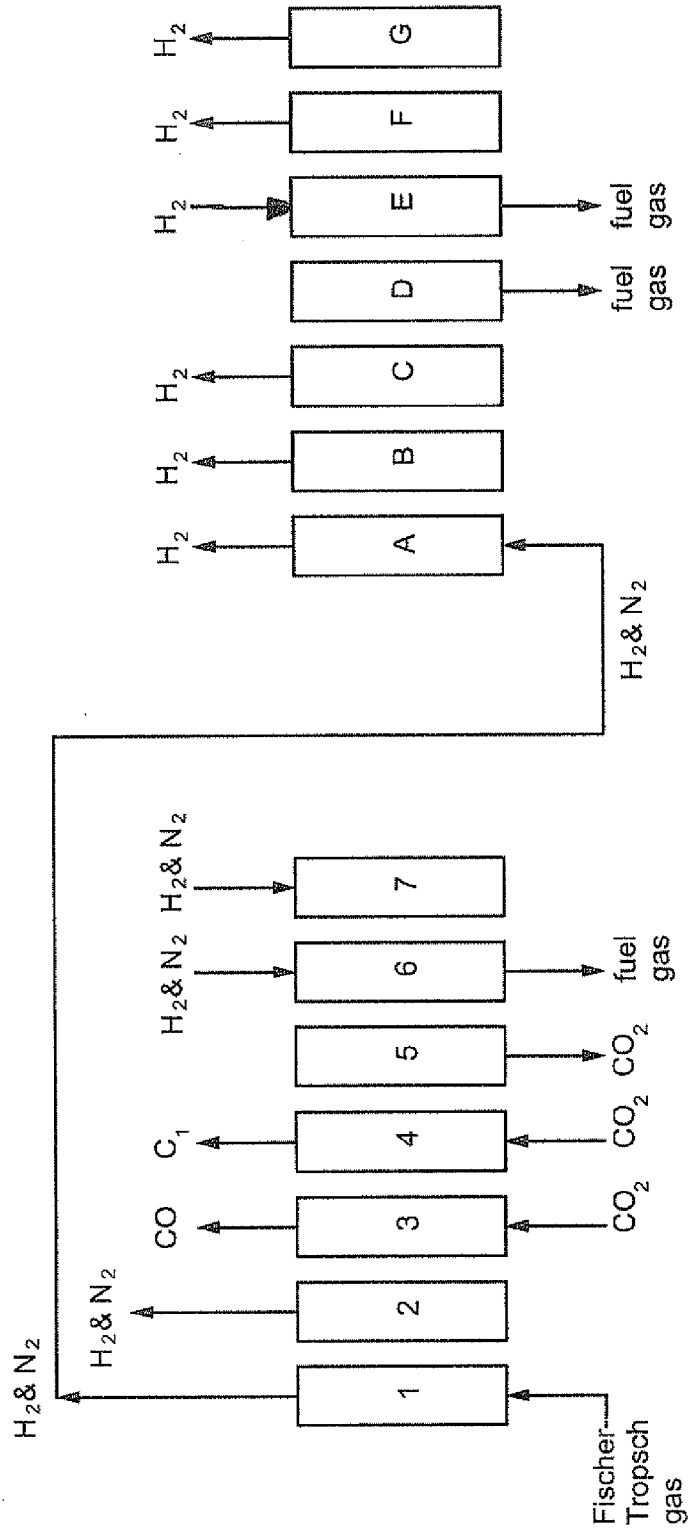
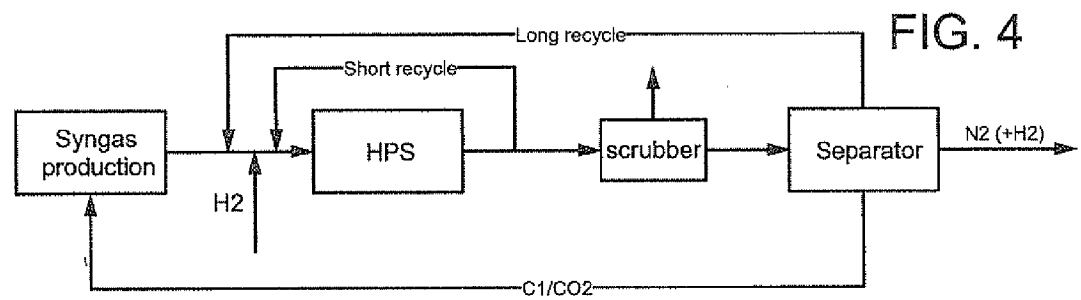
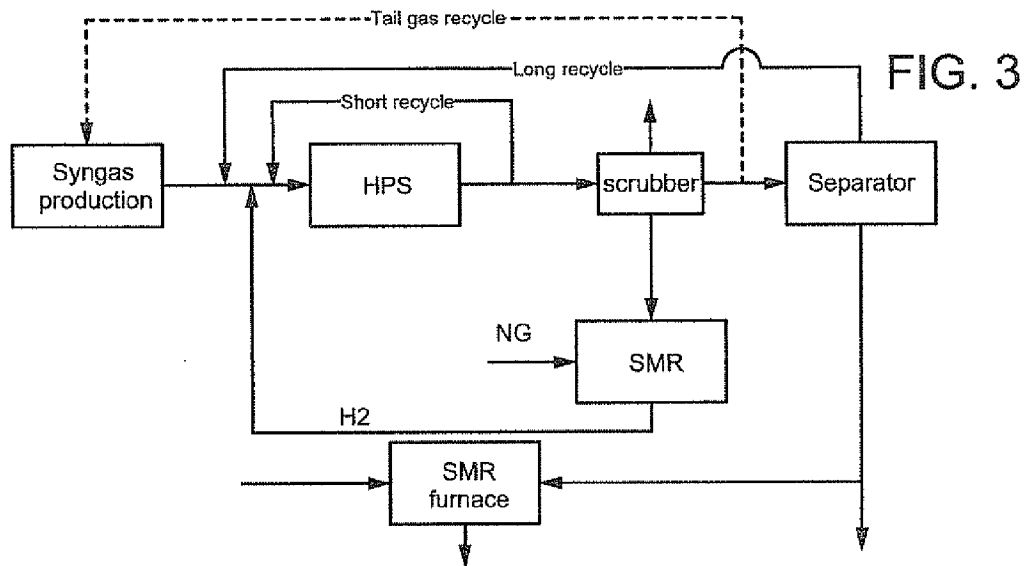
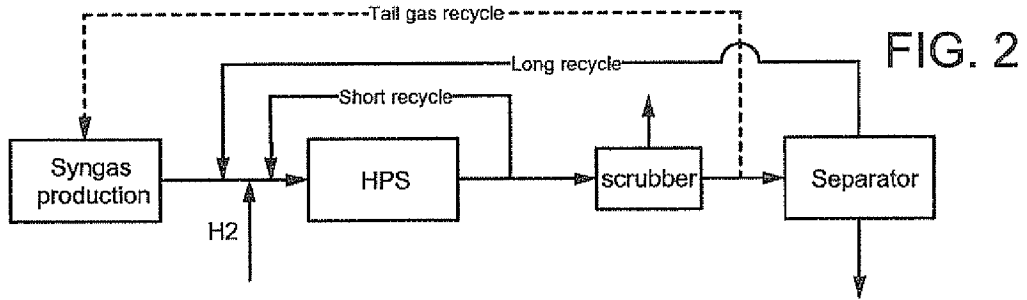


FIG. 1 B





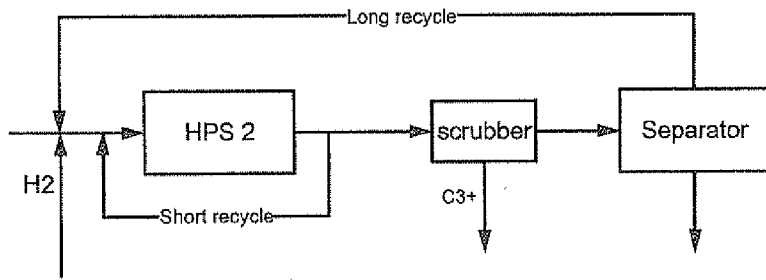


FIG. 5

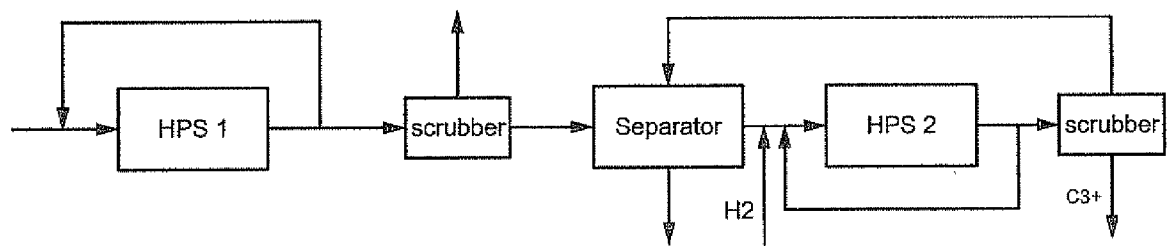


FIG. 6

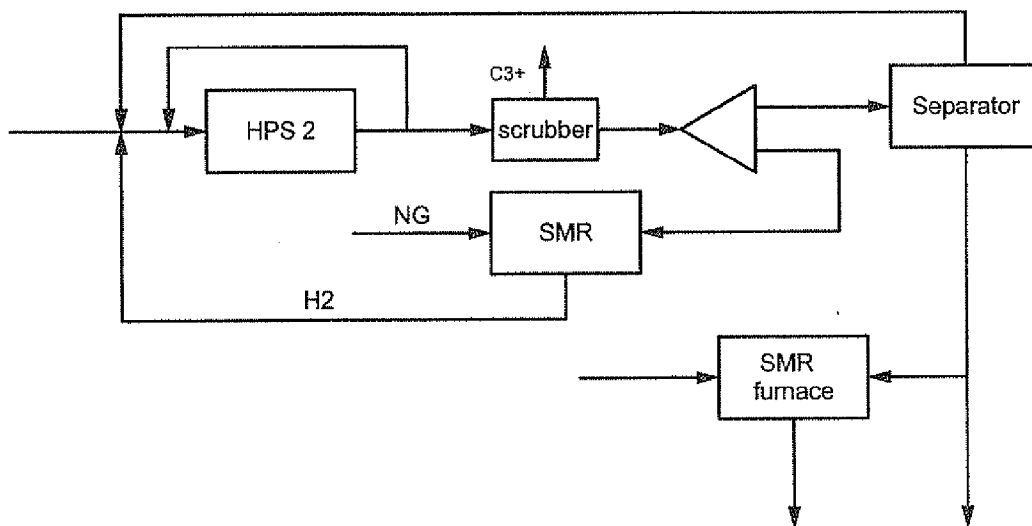


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/071188

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01D53/04 B01D53/047 C10K1/32 C01B3/56
 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)
 B01D C01B C10K

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 993 517 A (CHEN YUDONG [US] ET AL) 30 November 1999 (1999-11-30) column 5, line 50 - column 6, line 11 column 6, line 50 - column 7, line 48 column 11, line 43 -----	1-14
A	US 2006/116430 A1 (WENTINK PAUL [FR] ET AL) 1 June 2006 (2006-06-01) the whole document -----	1-14
A	US 6 045 603 A (CHEN YUDONG [US] ET AL) 4 April 2000 (2000-04-04) the whole document -----	1-14
A	US 4 726 816 A (FUDERER ANDRIJA [BE]) 23 February 1988 (1988-02-23) the whole document -----	1-14

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
---	---

Date of the actual completion of the international search 21 December 2012	Date of mailing of the international search report 07/01/2013
---	--

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 Gzil, Piotr
--	---------------------------------------

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2012/071188

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 5993517	A	30-11-1999	GB 2335378 A US 5993517 A	22-09-1999 30-11-1999
US 2006116430	A1	01-06-2006	AU 2004230996 A1 CA 2521078 A1 CN 1774493 A FR 2853904 A1 RU 2334780 C2 US 2006116430 A1 WO 2004092306 A1	28-10-2004 28-10-2004 17-05-2006 22-10-2004 27-09-2008 01-06-2006 28-10-2004
US 6045603	A	04-04-2000	EP 1101522 A1 US 6045603 A	23-05-2001 04-04-2000
US 4726816	A	23-02-1988	NONE	