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Remarks:
Claims 15, 16 and 17 are deemed to be abandoned due to non-payment of the claims fees (Rule 31 (2) EPC).

(54) **Fischer-Tropsch process**

(57) A process for the production of hydrocarbon products from syngas, in one or more syngas conversion reactors, the reactor(s) having a syngas entry stream system comprising one or more entry streams into the reactor(s) having an overall hydrogen/carbon monoxide $[H_2/CO]_{in}$ ratio below the syngas consumption ratio of the reactor(s), and an exit stream system comprising one or more exit streams from said reactor(s) having an overall $[H_2/CO]_{out}$ ratio lower than the $[H_2/CO]_{in}$ ratio, wherein a hydrogen stream is added to at least one of the entry streams to influence the $H_2/CO$ ratio in at least one entry stream such that the CO conversion ratio in the entry stream connected reactor(s) is in the range 70-95%.

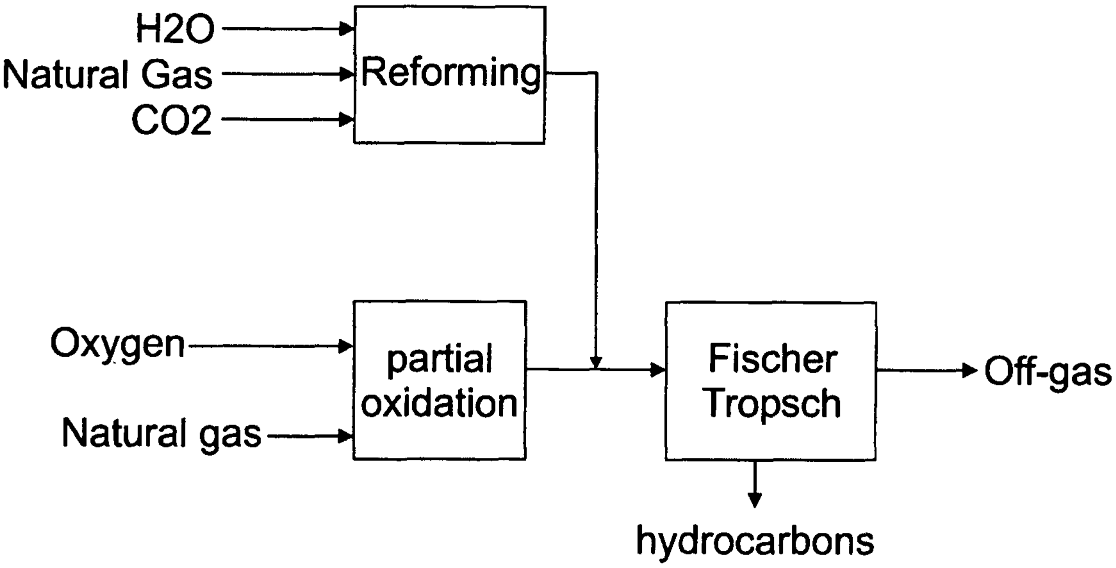

*Fig. 1*

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## Description

**[0001]** The present invention relates to a process for the production of hydrocarbon products from syngas, in particular a Fischer-Tropsch process.

**[0002]** Various processes are known for the conversion of gaseous hydrocarbonaceous feedstocks, especially methane from natural sources, for example natural gas, associated gas and/or coal bed methane, into liquid products, especially methanol and liquid hydrocarbons, particularly paraffinic hydrocarbons. At ambient temperature and pressure these hydrocarbons may be gaseous, liquid and (often) solid. Such processes are often required to be carried out in remote and/or offshore locations, where no direct use of the gas is possible. Transportation of gas, for example through a pipeline or in the form of liquefied natural gas, requires extremely high capital expenditure or is simply not practical. This holds true even more in the case of relatively small gas production rates and/or fields. Re-injection of gas will add to the costs of oil production, and may, in the case of associated gas, result in undesired effects on crude oil production. Burning of associated gas has become an undesirable option in view of depletion of hydrocarbon sources and air pollution. A process often used for the conversion of carbonaceous feedstocks into liquid and/or solid hydrocarbons is the well-known Fischer-Tropsch process.

**[0003]** The Fischer-Tropsch process can be used for the conversion of hydrocarbonaceous feed stocks into liquid and/or solid hydrocarbons. The feed stock (for example natural gas, associated gas, coal-bed methane, residual (crude) oil fractions or coal) is converted in a first step into a mixture of hydrogen and carbon monoxide (this mixture is referred to as synthesis gas or syngas). The syngas is then converted in one or more steps 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.

**[0004]** The hydrocarbonacaceous feed suitably is methane, natural gas, associated gas or a mixture of $C_{1-4}$ hydrocarbons. The feed comprises mainly, i.e. more than 90v/v%, especially more than 94%, $C_{1-4}$ hydrocarbons, and especially comprises at least 60 v/v percent methane, preferably at least 75%, more preferably 90%. Very suitably natural gas or associated gas is used. Suitably, any sulphur in the feedstock is removed.

**[0005]** Depending on the catalyst and the process conditions used in the Fischer-Tropsch reaction, normally gaseous hydrocarbons, normally liquid by hydrocarbons and optionally normally solid hydrocarbons are obtained. It is often preferred to obtain a large fraction of normally solid hydrocarbons. These solid hydrocarbons may be obtained up to 85 wt% based on total hydrocarbons, usually between 50 and 75 wt%.

**[0006]** The partial oxidation of gaseous feedstocks, producing mixtures of especially carbon monoxide and hydrogen, can take place according to various established processes. 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.

**[0007]** Generally, the partial oxidation process looks to convert natural gas, which is mainly methane, to the carbon monoxide and hydrogen mixture known as syngas. Pure methane would create a theoretical hydrogen to carbon monoxide (hereinafter termed "$H_2/CO$") molar ratio of 2, but because natural gas includes other compounds such as ethane, and because sometimes excess oxygen is used to try and achieve substantial, close or near 100% conversion of the methane, the actual $H_2/CO$ ratio in syngas is usually less than 2, such as 1.7-1.8.

**[0008]** The Fischer-Tropsch (FT) process may be operated in a single pass mode ("once through") or in a recycle mode. In either configuration, there is a syngas entry stream system into the process reactor or reactors, and naturally it is desired to obtain an overall CO conversion level or percentage as high as possible. However, there are operational constraints for the FT process. One of the operational constraints for the syngas conversion is the $H_2/CO$ ratio in the exit stream at the reactor outlet. A too low $H_2/CO$ ratio results in the loss of catalyst activity, e.g. by coke formation which may be permanent. In general, the criterion for the average $H_2/CO$ ratio in the exit stream at the reactor outlet(s) is desired to be $\geq 0.4$.

**[0009]** A consequence of this criterion is that there is a limit to the CO conversion level in the reactor(s) as the $H_2/CO$ ratio in the fresh syngas is smaller than the overall usage ratio. The overall usage ratio (UR) is the overall reaction stoichiometry of $H_2$ and CO in the Fischer-Tropsch reaction, including the water gas shift reaction. The correlation between the CO conversion level ($X_{co}$), the $H_2/CO$ ratio in the fresh syngas, the overall usage ratio and the $H_2/CO$ ratio in the outlet is formula (I):

$$X_{CO} = \frac{(H_2/CO)_{in} - (H_2/CO)_{out}}{UR - (H_2/CO)_{out}} \qquad (I)$$

As the overall usage ratio UR is relatively constant (typical value 2.04), the maximum CO conversion level $X_{CO}$ in the reactor is fixed by the $H_2$/CO ratio of the fresh syngas and the minimum $H_2$/CO outlet ratio. Thus there is very little flexibility to adjust the $H_2$/CO ratio without significantly affecting the efficiency. If the $H_2$/CO ratio of the fresh syngas is lower than design (e.g. 1.8), this immediately results in a limited CO conversion level and thus STY level. If for example the $H_2$/CO ratio in the fresh syngas is only 1.7, the maximum CO conversion level drops from 84% to 78%, a significant decrease in a large industrial process.

**[0010]** It is an object of the present invention to provide an improved syngas to hydrocarbon products process.

**[0011]** Accordingly, the present invention provides a process for the production of hydrocarbon products from syngas in one or more syngas conversion reactors, the reactor(s) having a syngas entry stream system comprising one or more entry streams into the reactor(s) having an overall hydrogen/carbon monoxide $[H_2/Co]_{in}$ ratio below the syngas consumption ratio of the reactor(s), and an exit stream system comprising one or more exit streams from said reactor(s) having an overall $[H_2/CO]_{out}$ ratio lower than the $[H_2/CO]_{in}$ ratio,
wherein a hydrogen stream is added to at least one of the entry streams to influence the $H_2$/CO ratio in said stream such that the CO conversion ratio in the reactor(s) is in the range 70-95%.

**[0012]** In general, the $[H_2/CO]_{in}$ ratio in the entry stream system is below the consumption ratio in a hydrocarbon forming process such as the Fischer-Tropsch reaction, and a low $[H_2/CO]_{in}$ ratio improves the $C_{5=}$ selectivity. Such a reaction, especially when using for example a cobalt catalyst, generally follows the equation:

$$CO + 2H_2 \rightarrow (-CH_2)_n - + H_2O$$

**[0013]** In the above, the theoretical $H_2$ to CO ratio is 2, although generally a slight excess of hydrogen is preferred to seek greater conversion of the carbon monoxide. The ratio of hydrogen to carbon monoxide actually used in the reactor by the process and calculated by analysis of the products formed is the "consumption ratio". In the present invention, the consumption ratio is generally below the above theoretical ratio of 2.

**[0014]** In one embodiment of the present invention, the overall $[H_2/CO]_{in}$ ratio of all the entry streams forming the entry stream system is in the range 1.6-2.0, preferably about 1.7-1.9.

**[0015]** In another embodiment of the present invention, the overall $[H_2/CO]_{out}$ ratio of all the exit streams forming the exit stream system is in the range 0.3-0.7, preferably about 0.4-0.5.

**[0016]** With a general $[H_2/CO]_{in}$ ratio in the range 1.6-2.0, the actual $H_2$/CO ratio of each stream of syngas as it enters a reactor is desired to be lower, generally in the range 1.0-1.4. This lowering of the $H_2$/CO ratio relates to the diffusion limitation involved in the Fischer-Tropsch conversion, wherein the hydrogen gas travels faster to the centre of catalyst-based supports compared to the larger carbon monoxide molecules, and a high $H_2$/CO ratio would result in a decrease of the $C_{5=}$ selectivity. Methods of reducing the $[H_2/CO]_{in}$ ratio prior to entry are well known in the art, such as mixing the syngas with other syngas having a lower $H_2$/CO ratio.

**[0017]** This $[H_2/CO]_{in}$ reduction could be partly achieved by the use of recycle of the product(s) from the reaction. For example, product having a $[H_2/CO]_{out}$ ratio of 0.4-0.5 can be used to reduce the $[H_2/CO]_{in}$ entry ratio.

**[0018]** The present invention includes adjustment of the $H_2$/CO ratio of the syngas through a second hydrogen rich syngas stream which can be mixed with the entry stream syngas, thereby increasing the operational flexibility in the CO conversion level and thereby increasing the STY. The hydrogen rich stream could be for example pure hydrogen or a hydrogen rich syngas, for example from a SMR process described below.

**[0019]** Adjustment of $H_2$/CO may be desired for several reasons. Variations in each of the parameters in formula (I) above can be desired for different, although sometimes interrelated, reasons. For example, whilst the UR figure can vary, it is desired to keep it relatively constant. Similarly, whilst the $X_{co}$ conversion level naturally varies, it is desired to keep this figure "stable", or at least as constant as possible. Meanwhile the $(H_2/CO)_{in}$ ratio can vary due to several factors, such as instability in the syngas supply. As mentioned above, a change in the $(H_2/CO)_{in}$ ratio from 1.8 to 1.7 results in a conversion level drop of approximately 6%. Assuming it is intended to maintain the greatest possible conversion level, or at least keep the conversion level at a stable figure, it is better to seek this by increasing the $(H_2/CO)_{in}$ ratio, for instance by the introduction of a hydrogen stream.

**[0020]** Similarly, it is generally desired to maintain the $(H_2/CO)_{out}$ ratio at a fixed level, to provide stability to the catalyst in the reactor(s). However, if the $(H_2/CO)_{out}$ ratio changes either involuntarily or for some desired reason, or this ratio becomes too low, which is also problematic as discussed above, then again alteration of the $(H_2/CO)_{in}$ ratio by the addition of a hydrogen stream compensates for variation (in the $(H_2/CO)_{out}$ ratio in the desire to maintain $X_{co}$ and UR figures relatively constant). The use of the hydrogen stream may not expected to be significant, and could be in the range 0-20% of the entry stream system volume, more preferably 5-10% thereof.

**[0021]** The hydrogen stream may be pure hydrogen, i.e. having >99% purity, and without carbon monoxide. Alternatively the hydrogen stream may only need to be sufficiently pure to provide the intended effect of the invention. Sources of partially, substantially or wholly pure hydrogen are known in the art. One source is a hydrogen manufacturing unit. Another source is Steam Methane Reforming (SMR), which provides a high $H_2$/CO ratio through the reaction:

$$2CH_4 + 2H_2O \rightarrow 2CO + 6H_2$$

**[0022]** The methane in the above reaction can be provided from natural gas, for example the same natural gas as is used to form the syngas. Whilst the above reaction gives a theoretical $H_2/CO$ ratio of 3, in fact secondary reactions such as the reaction between carbon monoxide and water, increase the hydrogen content, and thus increase the $H_2/CO$ ratio.

**[0023]** Preferably, where a SMR product stream is used, it is used directly as the hydrogen stream, without any further treatment, for example purification.

**[0024]** Optionally, some of the CO in any hydrogen manufacturing process, such as SMR, could be removed.

**[0025]** In one embodiment of the present invention, the hydrogen stream has a $H_2/CO$ ratio greater than 3, preferably in the range of 4 to 8, more preferably 5 to 7.

**[0026]** Preferably the Xco conversion level is greater than 80%, and more preferably greater than 85%.

**[0027]** The present invention could involve a multi-stage conversion process which may involve, two, three, or more conversion stages, generally two. Generally, the CO conversion level for each stage of a multi-stage process of the present invention is approximately the same.

**[0028]** In a multi-stage process, a hydrogen stream could be added to at least one entry streams for one, more than one, or each stage, to influence the $H_2/CO$ ratio in the at least one entry stream for the relevant stage(s). The type and amount of hydrogen stream for each relevant stage may be the same or different to the type and amount of hydrogen stream(s) for each other stage.

**[0029]** Preferably, the CO conversion level during each stage of a multi-stage conversion process is in the range 70-95%, and more preferably about 80-95%. Using a two stage process, a 80% CO conversion level at each stage provides an overall approximate 96% CO conversion level.

**[0030]** In the present invention, the process may be carried out in one or more parallel reactors, such parallel reactors generally being provided with the same syngas entry stream, and one or more of the reactors possibly being provided by two or more entry streams.

**[0031]** One or more of the entry streams may be derived from a common source, and one or more of the exit streams may be combined.

**[0032]** The term "entry stream system" refers the combined parameters of all the entry stream(s), which may still be physically distinct. Similarly, the term "exit stream system" refers to the combined parameters of all the exit stream(s).

**[0033]** In one embodiment of the present invention, all the entry streams for the process are derived from a single source of syngas.

**[0034]** The present invention also provides a hydrocarbon product or products whenever formed by a process as herein described, including any products made by hydrocoversion of the hyrocarbon product(s). In particular, the present invention provides products generally formed by the Fischer-Tropsch process.

**[0035]** Products of the Fischer-Tropsch synthesis may range from methane to heavy paraffinic waxes. Preferably, the production of methane is minimised and a substantial portion of the hydrocarbons produced have a carbon chain of at least 5 carbon atoms. Preferably, the amount of $C_{5+}$ hydrocarbons is at least 60% by weight of the total product, more preferably, at least 70% by weight, even more preferably, at least 80% by weight, most preferably, at least 85% by weight.

**[0036]** Fischer-Tropsch catalysts are known in the art, and typically include a Group VIII metal component, preferably cobalt, iron and/or ruthenium, more preferably cobalt. Typically, the catalysts comprise a catalyst carrier. The catalyst carrier is preferably porous, such as a porous inorganic refractory oxide, more preferably alumina, silica, titania, zirconia or mixtures thereof.

**[0037]** References to the Periodic Table 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 (CPC Press).

**[0038]** The optimum amount of catalytically active metal present on the carrier depends *inter alia* on the specific catalytically active metal. Typically, the amount of cobalt present in the catalyst may range from 1 to 100 parts by weight per 100 parts by weight of carrier material, preferably from 10 to 50 parts by weight per 100 parts by weight of carrier material.

**[0039]** The catalyst suitably has an average diameter of 0.5-15 mm. One form of catalyst is as an extrudate. Such extrudates suitably have a length of 2-10mm, especially 5-6mm, and a cross section suitably of 1-6mm$^2$, especially 2-3mm$^2$.

**[0040]** The catalytically active metal may be present in the catalyst together with one or more metal promoters or cocatalysts. The promoters may be present as metals or as the metal oxide, depending upon the particular promoter concerned. Suitable promoters include oxides of metals from Groups IIA, IIIB, IVB, VB, VIB and/or VIIB of the Periodic Table, oxides of the lanthanides and/or the actinides. Preferably, the catalyst comprises at least one of an element in Group IVB, VB and/or VIIB of the Periodic Table, in particular titanium, zirconium, manganese and/or vanadium. As an alternative or in addition to the metal oxide promoter, the catalyst may comprise a metal promoter selected from Groups VIIB and/or VIII of the Periodic Table. Preferred metal promoters include rhenium, platinum and palladium.

**[0041]** A most suitable catalyst comprises cobalt as the catalytically active metal and manganese and/or vanadium as a promoter.

**[0042]** The promoter, if present in the catalyst, is typically present in an amount of from 0.1 to 60 parts by weight per 100 parts by weight of carrier material. It will however be appreciated that the optimum amount of promoter may vary for the respective elements which act as promoter. If the catalyst comprises cobalt as the catalytically active metal and manganese and/or vanadium as promoter, the cobalt: (manganese + vanadium) atomic ratio is advantageously at least 12:1.

**[0043]** The Fischer-Tropsch synthesis is preferably carried out at a temperature in the range from 125°C to 350°C, more preferably 175°C to 275°C, most preferably 200°C to 260°C. The pressure preferably ranges from 5 to 150 bar abs., more preferably from 5 to 80 bar abs.

**[0044]** The gaseous hourly space velocity may vary within wide ranges and is typically in the range from 500 to 10,000 N1/1/h, preferably in the range from 1000 to 4,000 N1/1/h.

**[0045]** It will be understood that the skilled person is capable to select the most appropriate conditions for a specific reactor configuration and reaction regime. These include possible recycling of formed products such as gases and waxes.

**[0046]** The present invention provides the use of a hydrogen stream to influence the $H_2$/CO ratio in a syngas entry stream into a Fischer-Tropsch reactor. As mentioned above, the hydrogen may not be pure hydrogen, and can be provided by various processes, such as the SMR process described above. Indeed, the use of SMR process provides a further benefit to the present invention. It provides an integrated process for syngas production and conversion of carbonaceous feedstocks to hydrocarbonaceous products (including for example light and heavy paraffins, methanol and the like). One of the advantages of such an integrated process is the ability to help balance the energy requirements/output of various steps of a Fischer-Tropsch plant overall system, and thus improve the overall efficiency (in terms of carbon efficiency and thermal efficiency) of the Fischer-Tropsch process as a whole.

**[0047]** A further advantage provided by the present invention is that in integrating the syngas production and SMR processes, there is a reduction in the overall demand for oxygen in a hydrocarbon product plant, as the oxygen required in the SMR reaction can be provided from a superheated steam of the syngas production.

**[0048]** Without wishing to be restricted to a particular embodiment, the invention will now be described in further detail with reference to the accompanying drawing in which:

Figure 1 is a schematic flow diagram of an embodiment of the present invention.

Figure 1 shows a suitable arrangement combining the use of natural gas into two streams, one for a reforming process and one for a partial oxidation process. The partial oxidation process may be the Shell Gasification Process (SGP) as hereinbefore described.

**[0049]** The $H_2$/CO ratio from the partial oxidation process is generally in the range 1.7-1.9, and this can be reduced to preferred ratio of 1.0-1.4 in two ways: (a) by the recycle of at least a portion of the exit stream from the reactor, and (b) introduction of a hydrogen stream.

**[0050]** The steam methane reforming process provides a high hydrogen-content stream, possibly having a $H_2$/CO ratio of 5 or 6. Reformed syngas can be used as a source of an enriched hydrogen stream, for example if the CO is removed by a suitable process such as pressure swing adsorption PSA.

**[0051]** The introduction of the hydrogen stream from the reforming process provides the ability to influence the $H_2$/CO ratio in the Fischer-Tropsch stream, especially to seek a constant and/or stable CO conversion level.

## Claims

**1.** A process for the production of hydrocarbon products from syngas, in one or more syngas conversion reactors, the reactor(s) having a syngas entry stream system comprising one or more entry streams into the reactor(s) having an overall hydrogen/carbon monoxide $[H_2/CO]_{in}$ ratio below the syngas consumption ratio of the reactor(s), and an exit stream system comprising one or more exit streams from said reactor(s) having an overall $[H_2/CO]_{out}$ ratio lower than the $[H_2/CO]_{in}$ ratio,
wherein a hydrogen stream is added to at least one of the entry streams to influence the $H_2$/CO ratio in at least one entry stream such that the CO conversion ratio in the entry stream connected reactor(s) is in the range 70-95%.

**2.** A process as claimed in claim 1 wherein the $[H_2/CO]_{in}$ ratio of the entry stream system is in the range 1.6-2.0.

**3.** A process as claimed in claim 2 wherein the $[H_2/CO]_{in}$ ratio of each entry stream is in the range 1.7-1.9.

**4.** A process as claimed in any one of the preceding claims wherein the $[H_2/CO]_{out}$ ratio of the exit stream system is in the range 0.3-0.7.

**5.** A process as claimed in claim 4 wherein the $[H_2/CO]_{out}$ ratio in the exit stream system is in the range 0.4-0.5.

**6.** A process as claimed in any one of the preceding claims involving two or more reactors operating in parallel.

**7.** A process as claimed in any one of the preceding claims wherein at least a portion of the exit stream system product is recycled into the entry stream system.

**8.** A process as claimed in any one of the preceding claims wherein the hydrogen stream has a $H_2/CO$ ratio greater than 3, optionally in the range of 4 to 8, more preferably 5 to 7.

**9.** A process as claimed in any one of the preceding claims wherein the hydrogen stream is provided by a steam methane reforming process.

**10.** A process as claimed in any one of claims 1 to 7 wherein the hydrogen steam is pure hydrogen.

**11.** A process as claimed in any one of the preceding claims wherein the CO conversion ratio is in the range 80-95%, preferably 85-95%.

**12.** A process as claimed in any one of the preceding claims wherein the process for the production of hydrocarbon products is a multi-stage conversion process involving 2-4 stages, preferably 2 stages.

**13.** A process as claimed in claim 12 wherein the CO conversion ratio for each stage is in the range 70-95%, preferably 80-95%, and more preferably 85-95%.

**14.** A process as claimed in any one of the preceding claims wherein the process includes a catalyst; preferably a catalyst comprising one or more metals from Group VIII of the Periodic Table, more preferably a non-shifting catalyst, preferably cobalt.

**15.** A process as claimed in any one of the preceding claims wherein the process is carried out at a temperature in the range from 125 to 350°C, preferably 200 to 260°C, and at a pressure in the range from 5 to 150 bar, preferably 5-80 bar.

**16.** A hydrocarbon product whenever produced by a process according to anyone of claims 1 to 15, including any products made by hydroconversion of the hydrocarbon product(s).

**17.** Use of a hydrogen stream to influence the $H_2/CO$ ratio in an entry stream for a Fischer-Tropsch process.

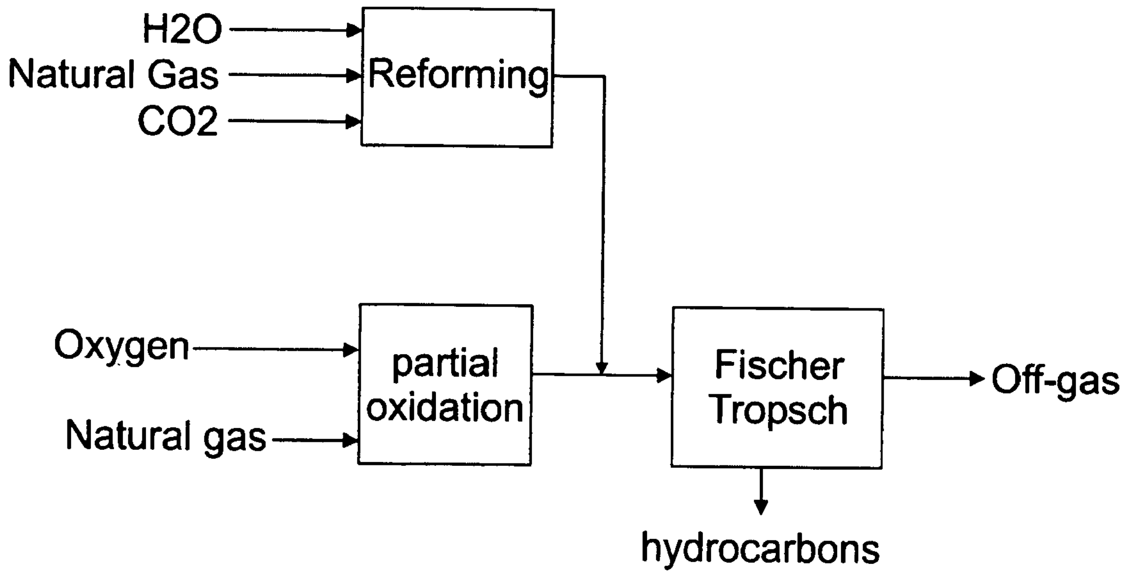
H2O
Natural Gas
CO2
Reforming
Oxygen
Natural gas
partial oxidation
Fischer Tropsch
Off-gas
hydrocarbons

*Fig. 1*

**European Patent Office**

# EUROPEAN SEARCH REPORT

Application Number
EP 05 25 4536

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
|---|---|---|---|
| X | WO 2004/026994 A (SASOL TECHNOLOGY LIMITED; STEYNBERG, ANDRE, PETER) 1 April 2004 (2004-04-01)<br>* claims 1,6-8,12,14; figure 1 *<br>* page 2, lines 21-24 *<br>* page 5, lines 28-32 *<br>* page 6, lines 20-29 *<br>* page 8, lines 6-29 *<br>* page 10, line 5 *<br>* page 11, lines 4-6,30-34 *<br>----- | 1-14 | C10G2/00<br>C01B3/34 |
| X | EP 0 178 007 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V) 16 April 1986 (1986-04-16)<br>* claims 1,3,5,6,8; figure *<br>* page 3, lines 23-30 *<br>* page 6, line 12 - page 7, line 16 *<br>----- | 1-14 | |
| X | US 6 310 108 B1 (BONNEAU REYNALD ET AL) 30 October 2001 (2001-10-30)<br>* claims 1,2; figure 2 *<br>* column 3, lines 11-32 *<br>* column 14, lines 10-26 *<br>----- | 1-14 | **TECHNICAL FIELDS SEARCHED (IPC)**<br>C10G<br>C01B |
| X | US 2004/014825 A1 (HENSMAN JOHN RICHARD) 22 January 2004 (2004-01-22)<br>* figure 1 *<br>* page 5, paragraph 51-55 *<br>----- | 1,6,8 | |
| X | US 2003/050348 A1 (KENNEDY PAUL EDWIN) 13 March 2003 (2003-03-13)<br>* claims 1-3; figure 1 *<br>* page 1, paragraph 12 *<br>* page 1, paragraph 17 - page 2, paragraph 17 *<br>* page 2, paragraph 25-27 *<br>* page 3, paragraph 30 *<br>-----<br>-/-- | 1-14 | |

~~The present search report has been drawn up for all claims~~

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| Munich | 25 November 2005 | Harf, J |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

**European Patent Office**

## EUROPEAN SEARCH REPORT

Application Number
EP 05 25 4536

### DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
|---|---|---|---|
| X | EP 1 219 566 A (L'AIR LIQUIDE, S.A. A DIRECTOIRE ET CONSEIL DE SURVEILLANCE POUR L'ETU) 3 July 2002 (2002-07-03)<br>* figure 1 *<br>* page 2, paragraph 5-7 *<br>----- | 1-14 | |
| | | | TECHNICAL FIELDS SEARCHED (IPC) |

~~The present search report has been drawn up for all claims~~

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| Munich | 25 November 2005 | Harf, J |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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EPO FORM 1503 03.82 (P04C01)

European Patent
Office

Application Number
EP 05 25 4536

## CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☒ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

11-14

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

## LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 25 4536

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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