(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 October 2014 (02.10.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/154389 A1

(51) International Patent Classification:
C01B 3/38 (2006.01)

(21) International Application Number:
PCT/EP2014/052646

(22) International Filing Date:
11 February 2014 (11.02.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2013 103 187.0 28 March 2013 (28.03.2013) DE

(71) Applicant: **L'AIR LIQUIDE SOCIÉTÉ ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCÉDÉS GEORGES CLAUDE** [FR/FR]; 75 quai d'Orsay, F-75007 Paris (FR).

(72) Inventors: **OELMANN, Tobias**; Eleonore-Sterling-Straße 56, 60433 Frankfurt am Main (DE). **MÜLLER, Dierk**; Zingelweg 3, 61184 Karben (DE). **GRONEMANN, Veronika**; Karl-Liebknecht-Straße 18e, 61184 Karben (DE).

(74) Agent: **KEIL & SCHAAFHAUSEN PATENT- UND RECHTSANWÄLTE**; Friedrichstrasse 2-6, 60323 Frankfurt am Main (DE).

(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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

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

(54) Title: PROCESS AND PLANT FOR PRODUCING SYNTHESIS GAS

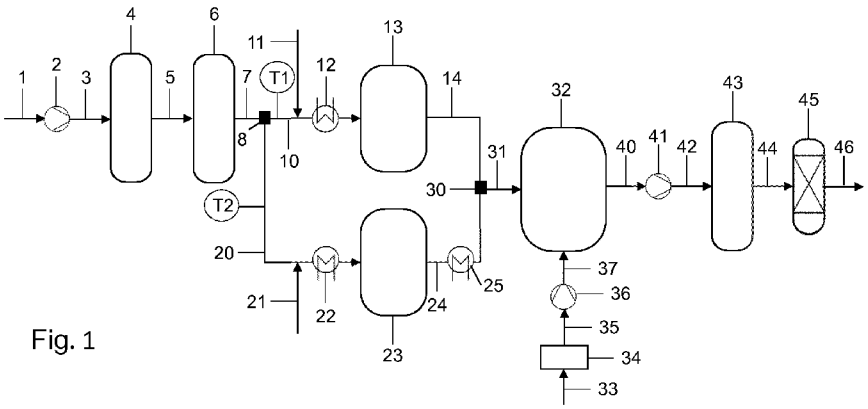


Fig. 1

(57) Abstract: For producing a synthesis gas containing hydrogen and carbon monoxide from a starting gas containing hydrocarbons, the starting gas is split up into a first partial stream (T1) and a second partial stream (T2), wherein the first partial stream (T1) is supplied to a steam reformer (13) in which it is catalytically converted together with steam to obtain a gas stream containing hydrogen and carbon oxides, wherein downstream the steam reformation the first partial stream (T1) is again combined with the second partial stream (T2), and wherein the combined gas stream is supplied to an autothermal reformer (32) in which the combined gas stream together with an oxygen-containing gas is autothermally reformed to a synthesis gas. The first partial stream (T1) is guided directly into the steam reformer (13) and the second partial stream (T2) is guided through a pre-reformer (23) before passing through the autothermal reformer (32).

WO 2014/154389 A1

Process and Plant for Producing Synthesis Gas

The present invention relates to a process for producing a synthesis gas containing hydrogen and carbon monoxide from a starting gas containing hydrocarbons, wherein a feed stream of the starting gas is split up into a first partial stream and a second partial stream, wherein the first partial stream is supplied to a steam reformer in which it is catalytically converted together with steam to obtain a gas stream containing hydrogen and carbon oxides, wherein downstream the steam reformation the first partial stream is again combined with the second partial stream to obtain an entire stream, and wherein the entire stream is supplied to an autothermal reformer in which it is autothermally reformed together with gas rich in oxygen to obtain a synthesis gas. The invention furthermore comprises a plant for carrying out the process.

In principle, all hydrogen-containing gas mixtures which can be used as starting substances of a synthesis reaction are referred to as synthesis gas. Typical syntheses for which synthesis gas is used are the methanol and the ammonia synthesis.

In principle, the production of synthesis gas can be effected from solid, liquid and gaseous starting substances. The most important gaseous synthesis gas production, the so-called reformation, utilizes natural gas as educt. Natural gas substantially is a mixture of gaseous hydrocarbons whose composition varies depending on the place of origin, wherein the main component always is methane (CH_4) and as further components higher hydrocarbons with two or more carbon atoms as well as impurities, e.g. sulfur, can be contained.

For reforming natural gas to synthesis gas the so-called steam reformation (also *steam reforming*) is used above all, in which on a catalyst the contained metha-

ne chiefly is converted into hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) according to the following reaction equations:

$$CH_4 + 3H_2O \leftrightarrow CO + 3H_2$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 .$$

When using a suitable catalyst and adding steam, higher hydrocarbons in addition are split up to methane according to the so-called rich gas reaction:

$$C_nH_m + \left(\frac{2-m}{2}\right)H_2O \leftrightarrow \left(n - \frac{2n-m}{4}\right)CH_4 + \frac{2n-m}{4}CO_2 .$$

The highly exothermal character of the methane conversion with water to carbon monoxide dominates the entire steam reformation. The energy input necessary for this endothermal process is realized via an external heating.

The methane conversion can be increased by increasing the S/C ratio (*steam to carbon ratio*), i.e. by hyperstoichiometric addition of steam.

In principle, synthesis gas also can be obtained from methane by partial oxidation. The partial oxidation of hydrocarbons is to be understood as incomplete combustion, in which above all hardly evaporable higher hydrocarbons can be converted completely. For the use of methane as educt the following gross reaction equation can be indicated:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 .$$

This main reaction of the partial oxidation is exothermal and is determined by the oxygen quantity to be added substoichiometrically.

The so-called autothermal reformation describes a mixed process of steam reformation and partial oxidation. In a suitable operating mode, the exothermal process (partial oxidation) and the endothermal process (steam reformation) are adjusted to each other such that no energy must be supplied to the system from outside.

What is problematic when using an autothermal reformer in particular is the presence of higher-valent hydrocarbons, as the same can undergo a multitude of both endothermal and exothermal reactions and thus, in dependence on the composition of the natural gas used, it can very quickly occur that the reaction no longer is conducted autothermally, but heat is produced or consumed. When the autothermal reaction develops into an endothermal reaction, the reaction space cools down, until the existing energy no longer is sufficient to provide the required activation energies, so that no more reaction takes place. When the reaction instead inadvertently proceeds exothermally, there is provided energy which leads to unwanted combustion processes, which in turn likewise are strongly exothermal, so that the reaction no longer proceeds in a controlled way. Both of this must be avoided at all costs.

For this purpose, a so-called pre-reformer generally is used, which converts at least parts of the gas stream used as educt already before the autothermal reformation. From the prior art, a multitude of possible combinations of pre-reformer, steam reformer, partial oxidation and autothermal reformation are known.

The most simple form of such combined reforming, as it is known for example from Ullmann's Encyclopedia of Industrial Chemistry, 6th edition, 1998, electronic release "7.1 Methanol Production from Natural Gas", completely omits a pre-reformer. Parts of the inlet stream are passed through a steam reformer, while

the remaining residual stream is guided in a bypass around this steam reformer. The steam-reformed and the untreated stream subsequently are combined and subjected to an autothermal reformation.

WO 2008/122391 A describes that the entire educt stream is guided through a pre-reformer and this pre-reformed stream subsequently is divided into three partial streams. These partial streams are supplied to an autothermal reformer, a gas-heated reformer and a steam reformer.

DE 10 2006 023 248 A1 also describes that the entire gas stream must be subjected to a pre-reformation. Downstream the pre-reformation, the pre-reformed gas stream is divided into two partial streams, of which the first partial stream is supplied to a steam reformation and after passing the steam reformation is subjected to an autothermal reformation together with the untreated second partial stream. This has the disadvantage that the entire stream is guided through the pre-reformer and the pre-reformer thus must be dimensioned correspondingly large, which distinctly increases the equipment and operating costs.

From EP 0 233 076 B1 it is known that it is possible to split up the natural gas into two streams. A partial stream first is passed through a correspondingly smaller pre-reformer and subsequently through the steam reformer, in which the natural gas together with steam is catalytically converted to a gas stream containing hydrogen and carbon oxides. After passing through the pre-reformer and the steam reformer, the first partial stream then is supplied to the downstream autothermal reformer. The second partial stream is guided past the steam reformer and supplied directly to the autothermal reformer. However, this involves the disadvantage that that partial stream which is guided directly into the autothermal reformer has not yet undergone any pretreatment. In particular when the natural gas contains a relatively high amount of higher-valent hydrocarbons,

particularly more than 5 % higher-valent hydrocarbons, quite particularly more than 10 % higher-valent hydrocarbons, the problem arises here that this partial stream cannot be heated to temperatures above 450 °C. An exceedance of this temperature would lead to carbonizations and hence to clogging of the conduits. The relatively low temperature to which this second partial stream maximally can be heated leads to a decrease of the mixing temperature of the two partial streams and thus to a decrease of the inlet temperature into the autothermal reformer. A lower operating temperature in the autothermal reformer, however, in turn leads to the fact that an increased quantity of carbon dioxide is produced and the amount of carbon monoxide decreases.

In addition, a lower inlet temperature into the autothermal reformer involves the risk that the so-called metal dusting occurs. Metal dusting is a form of corrosion, in which a graphite layer is deposited on the surface of the metal, whereby metal carbon tips are formed, which leads to a degradation of the metal body. This graphite layer is formed of carbon which occurs due to a shift of the Boudouard equilibrium.

According to Boudouard, the reaction

$$CO_2 + C \rightarrow 2CO$$

is an equilibrium reaction which largely depends on the temperature and the partial pressures of CO and CO_2. Due to the endothermal reaction, high temperatures shift the equilibrium to the product side (CO), and an increase in pressure shifts the equilibrium to the side of the educts. When the temperature falls below the Boudouard temperature, the reaction proceeds in the direction CO_2 + C. The resulting elementary carbon leads to metal dusting and thus to a considerable damage of the equipment. To avoid this, the temperature of the process gas must lie above the Boudouard temperature (under the process

conditions about 670 °C), which by setting the temperature of the second partial stream to a maximum of 450 °C only can be effected when the fraction of the second partial stream is kept correspondingly low, in particular below 50 %. However, this distinctly limits the flexibility of the process with regard to splitting up the two partial streams, since the composition of the resulting synthesis gas no longer is freely adjustable by the fractions of the respective partial streams.

Therefore, it is the object of the present invention to provide for the production of synthesis gas with freely selectable hydrogen-to-carbon ratio, in which it is also possible to use natural gas with a high content of hydrocarbons with a chain length of >= 2 carbon atoms for the synthesis of a gas rich in carbon monoxide, and the apparatus and operational expenditure is minimized at the same time.

According to the invention, this object is solved by a process with the features of claim 1.

For this purpose, a feed stream of the starting gas is split up into a first partial stream and a second partial stream. The first partial stream is supplied directly to a steam reformer, in which it is catalytically converted together with steam to obtain a gas stream containing hydrogen and carbon oxides. After passing the steam reformation, the first partial stream is combined with the second partial stream and this entire gas stream is passed into an autothermal reformer, where it is reformed together with gas rich in oxygen to obtain a synthesis gas. Upstream the autothermal reformation, the second partial stream is supplied to a pre-reformer, while the first partial stream only passes the steam reformer and no pre-reformer. By acting against the opinion held so far in the prior art that the steam reformer definitely requires a pre-reformer, the pre-reformer can be saved for the steam reformer, whereby the additional apparatus and operational expenditure of the process is reduced distinctly. At the same time, the process nevertheless can also be operated with natural gas which contains a distinct

fraction of higher-valent hydrocarbons, since before entry into the autothermal reformer the second partial stream is subjected to the pre-reformation and higher-valent hydrocarbons thus are largely removed, which actually provides for heating to temperatures above 450 °C without the risk of carbonizations.

Beside the distinctly smaller pre-reformer and the resulting economic savings, the process also has the advantage that it provides for an increased flexibility with respect to the partial streams to be set, and the first partial stream thus can take any value between > 0 and < 100 vol-% of the entire stream, and the second partial stream correspondingly is calculated as difference between entire stream and partial stream.

It is particularly favorable when in the pre-reformer those reactions exclusively take place which convert higher-valent hydrocarbons with two or more C atoms in their chains to carbon dioxide and methane according to the rich gas reaction. A conversion of the methane to synthesis gas should however be avoided. Preferably 90 wt-%, particularly preferably 95 wt-% and quite particularly preferably 99 wt-% of the higher-valent hydrocarbons are converted to methane and carbon dioxide. The conversion of methane in the pre-reformer accordingly should be < 5 wt-%, preferably < 1 wt-%. In the flow sheet according to the invention, the amounts of hydrogen and carbon monoxide obtained thereby are influenced only by the steam reformer and the autothermal reformer.

It is furthermore advantageous that with this process the composition of the synthesis gas obtained practically can be varied as desired due to the increased flexibility. For the methanol synthesis, for example a stoichiometric number (SZ) of 2.0 to 2.1 is required, the stoichiometric number for the methanol synthesis being defined by to the following formula:

$$SZ = \frac{H_2 - CO_2}{CO + CO_2}.$$

In principle, the steam reformer increases the stoichiometric number, since more hydrogen is produced; whereas the autothermal reformer decreases the stoichiometric number, since less hydrogen and a higher fraction of carbon oxides is obtained.

In that no pre-reformer is provided upstream of the steam reformer, the reaction taking place can distinctly be improved with regard to the stoichiometric number, so that the following applies for the steam reformer:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

which in simple terms results in a stoichiometric number of 3. For the autothermal reformer, the stoichiometric number approximately is 1, since in simple terms the following reaction equation can be assumed:

$$CH_4 + O_2 \rightarrow CO + H_2O + H_2.$$

In the pre-reformer, the higher-valent hydrocarbons are converted into methane. In the steam reformer, on the other hand, a conversion directly to synthesis gas is effected with higher-valent hydrocarbons. Depending on the ratio of stoichiometric numbers SZ to be achieved, the two partial streams thus can be defined independent of the higher-valent natural gas contained in them.

What is also favorable in such a flow sheet is the possibility opening up for the start-up of the plant, which becomes difficult in that typically the catalysts used in the steam and pre-reformer are active only in reduced form, but - in particular when they are nickel-based - are available on the market only in oxidized form.

In the present procedure, the catalyst of the steam reformer first can be reduced, and subsequently the steam reformer can be put into operation. The feed stream of the starting gas is completely guided over the steam reformer, while the bypass stream amounts to 0 vol-%. The gas withdrawn from the steam reformer is supplied to a PSA plant (*Pressure Swing Adsorption*), in which the hydrogen obtained in the steam reformer is purified by pressure swing adsorption. The hydrogen thus obtained then is supplied to the pre-reformer for the reduction of its catalyst. After the reduction, the two partial streams then can assume values between 0 and 100 vol-%, and the autothermal reformation can be switched in.

To reliably avoid metal dusting in the second partial stream after the exit from the pre-reformer, it was found to be advantageous when the temperature after the pre-reformer lies between 650 and 800 °C.

To reliably avoid metal dusting in the combined entire gas stream, the temperature of the entire gas stream should lie above 630 °C, preferably between 660 and 800 °C.

Furthermore, it was found to be advantageous to heat the first partial stream before entry into the steam reformer to a temperature between 500 and 600 °C and/or the second partial stream before entry into the pre-reformer to a temperature between 400 and 500 °C. This ensures optimum operating conditions, whereby high conversions are obtained in the steam reformer, whereas in the pre-reformer exclusively the hydrocarbons with two or more carbon atoms are converted.

In addition, the catalysts for the pre-reformer and the steam reformer likewise are to be defined such that in the steam reformer high conversions equally are achieved for methane and for higher-valent hydrocarbons, whereas in the pre-

reformer exclusively carbon compounds with two or more carbon atoms are to be converted to hydrogen, carbon monoxide, carbon dioxide and methane. Therefore, it is recommendable to use a catalyst in the pre-reformer with a nickel content between 20 and 50 wt-%, preferably between 30 and 40 wt-%, whereas the catalyst in the steam reformer has a nickel content between 5 and 10 wt-%, preferably 7.5 to 8.5 wt-%. Preferably, for at least one of the catalysts Al_2O_3 is used as support.

During the procedure of the reforming reaction according to the invention the reaction temperature in the pre-reformer lies between 400 and 500 °C, whereas the reaction temperature in the steam reformer lies between 600 and 800 °C.

It is also favorable to adiabatically operate the pre-reformer, i.e. that here the system is transferred from one state into another, without thermal energy being exchanged with the surroundings. In the adiabatic reaction control the reaction temperature rises linearly with the conversion, so that the gas exiting from the pre-reformer already has a temperature at which metal dusting reliably is avoided. Preferably, the exit temperature from the pre-reformer lies between 650 and 800 °C. Then, no further heating is necessary any more.

The invention furthermore comprises a plant for the production of a synthesis gas containing hydrogen and carbon monoxide with the features of claim 11, which is suitable for carrying out the process mentioned above. Such plant comprises a splitter which splits up the starting gas into a first partial stream and a second partial stream. Furthermore, the plant comprises a steam reformer in which the first partial stream is catalytically converted with steam to obtain a gas stream containing hydrogen and carbon oxides, and an autothermal reformer in which the first partial stream guided over the steam reformer as well as the second partial stream are autothermally reformed together with gas rich in oxygen. It is decisive that the first partial stream is guided via a conduit from the

splitter directly into the steam reformer and the second partial stream is guided via a pre-reformer into the autothermal reformer. This results in the fact that the partial stream of the steam reformation no longer must be subjected to a pre-reformation, whereby the apparatus and operational expenditure can be reduced distinctly.

The pre-reformer preferably is operated adiabatically with an upstream preheating. The steam reformer is heated with a fired heater from the outside.

It is advantageous to provide a heat exchanger both in the conduit which guides the first partial stream from the splitter into the steam reformer and in the conduit which guides the second partial stream into the pre-reformer, so that the inlet temperature of the two streams can be adjusted individually for the respective process to be carried out.

Further developments, advantages and possible applications of the invention can also be taken from the following description of an exemplary embodiment and the drawing. All features described and/or illustrated form the subject-matter of the invention per se or in any combination, independent of their inclusion in the claims or their back-references.

In the drawing:

Fig. 1 schematically shows the process according to the invention for the production of synthesis gas.

Fig. 1 schematically illustrates the procedure of the process according to the invention for the production of synthesis gas in a process flow diagram. Natural gas is introduced into a compressor 2 via conduit 1 and then via conduit 3 into a hydrogenation 4. There, the natural gas is treated with hydrogen on a suitable

catalyst, e.g. a nickel catalyst, so that saturated hydrocarbon compounds are obtained.

Via conduit 5, the gas thus obtained is supplied to a desulfurization 6, from which the entire stream gets into a splitter 8 via conduit 7.

In the splitter 8, the entire stream is split up into the partial streams T1 and T2. The first partial stream T1 is supplied to the steam reformer 13 via conduit 10, wherein steam initially is admixed to the partial stream T1 via conduit 11 and in the heat exchanger 12 the resulting mixed stream then is brought to the required inlet temperature for the steam reformer 13. In the reactor 13, steam reforming of the pretreated natural gas is performed. Via conduit 14, the steam-reformed gas subsequently is transferred into a mixing zone 30.

The second partial stream T2 is guided from the splitter 8 via conduit 20 into a pre-reformer 23. For carrying out the pre-reformation, steam is admixed to the partial stream T2 via conduit 21 and the resulting second mixed stream is heated to the required inlet temperature in the heat exchanger 22. The exit stream of the pre-reformer 23 likewise is transferred into the mixer 30 via conduit 24, wherein the stream is heated even further in the heat exchanger 25 downstream of the pre-reformer 23, so that the two streams T1 and T2 are supplied to the mixing system 30 preferably with a similar temperature, particularly preferably with a temperature difference of <= 20 °C, so that no mixing problems occur.

From the mixing zone 30 the resulting new entire stream is fed into the autothermal reformer 32 via conduit 31. For operating the autothermal reformer 32, air is introduced into an air separation 34 via conduit 33, and the oxygen obtained there is fed into the autothermal reformer 32 via conduit 35, the condenser 36 and conduit 37. Via conduit 40, the product gas obtained in the reactor 32 is

withdrawn. Additional water and/or CO_2 likewise can be introduced into the reformer 32.

By way of example, Fig. 1 shows that the product gas from conduit 40 can be supplied to a methanol synthesis 43 via a compressor 41 and conduit 42, and then via conduit 44 to a methanol distillation 45, from which methanol finally can be withdrawn via conduit 46. Of course, a number of other syntheses, e.g. the ammonia synthesis or the Fischer-Tropsch process equally can be provided downstream of the reforming process.

As in the flow sheet according to the invention a certain ratio of stoichiometric numbers easily can be adjusted independent of the composition of the natural gas, it is also possible to offer a plurality of synthesis processes subsequent to the reformation, for which the ratio of stoichiometric numbers each can be adjusted individually.

Example

The following example shows the composition of the individual streams and the associated process parameters.

Process stream	**Starting gas**		**Partial stream T1 upstream steam reformer**		**Partial stream T1 downstream steam reformer**		**Partial stream T2 before pre-reformer**	
Phase	gaseous		gaseous		gaseous		gaseous	
Composition	kmol/h	mol-%	kmol/h	mol-%	kmol/h	mol-%	kmol/h	mol-%
CO_2	18.7	0.43	9.4	0.11	620.8	6.01	9.4	0.21
CO	5.3	0.12	2.6	0.03	412.3	3.99	2.6	0.06
H_2	129.9	3.00	64.9	0.78	3632.7	35.1	64.9	1.49
CH_3OH	0.9	0.02	0.4	0.01		4	0.4	0.01
H_2O	0.1	0.00	6130.7	73.9	4498.6		2189.5	50.29
O_2				1		43.5		
N_2	6.8	0.16	3.4		3.4	2	3.4	0.08
Aromatics	1.6	0.04	0.8	0.04	0.8		0.8	0.02
CH_4	4	92.7	2007.3	0.01	1168.4	0.03	2007.3	46.11
C_2H_6	4014.6	5	55.6	24.2		0.01	55.6	1.28
C_3H_8	111.2	2.57	11.8	0		11.3	11.8	0.27
C_4H_{10}	23.7	0.55	5.0	0.67		0	5.0	0.11
C_5H_{12}	10.0	0.23	2.3	0.14			2.3	0.06
C_6H_{14}	4.6	0.11	0.6	0.06			0.6	0.01
C_7H_{16}	1.2	0.03		0.03				
				0.01				
Total molar flow rate (kmol/h)	4328.5		8294.9		10337.1		4353.7	
	71236		146108		146108		75107	
Total mass flow rate [kg/h]	4982		13377		23225		6533	
Current volumetric flow rate (m^3/h)								
Temperature (°C)	375		560		760		480	
Pressure (bar (abs))	47.50		42.50		38.50		41.50	
Density (kg/m^3)	14.32		10.92		6.29		11.50	
Mol. weight	16.48		17.61		14.13		17.25	

Process stream	**Partial stream T2 upstream pre-reformer**		**Partial stream T2 downstream pre-reformer**		**combined gas stream**	
Phase	gaseous		gaseous		V gaseous	
Composition	kmol/h	mol-%	kmol/h	mol-%	kmol/h	mol-%
CO_2	89.2	1.98	89.2	1.98	710.0	4.78
CO	1.6	0.04	1.6	0.04	414.0	2.79
H_2	274.5	6.09	274.5	6.09	3907.2	26.31
CH_3OH						
H_2O	2031.2	45.02	2031.2	45.02	6529.8	43.98
O_2						
N_2	3.4	0.028	3.4	0.08	6.8	0.05
Aromatics	0.8	0.02	0.8	0.02	1.6	0.01
CH_4	2110.7	46.78	2110.7	3279.1	3279.1	22.08
C_2H_6						
C_3H_8						
C_4H_{10}						
C_5H_{12}						
C_6H_{14}						
C_7H_{16}						
Total molar flow rate (kmol/h)		4511.5		4511.5		14848.5
Total mass flow rate [kg/h]		75107		75107		221216
Current volumetric flow rate (m^3/h)		6635		9034		31682
Temperature (°C)		446		650		708
Pressure (bar (abs))		40.50		38.50		38.50
Density (kg/m^3)		11.32		8.31		6.98
Mol. weight		16.65		16.65		14.90

Standard steam flow (Nm^3/h) based on 0 °C and 101.25 Pa

List of Reference Numerals

1	conduit
2	compressor
3	conduit
4	hydrogenation
5	conduit
6	desulfurization
7	conduit
8	splitter
10, 11	conduit
13	steam reformer
14	conduit
20, 21	conduit
22	heat exchanger
23	pre-reformer
24	conduit
25	heat exchanger
30	mixing zone
31	conduit
32	autothermal reformer
33	conduit
34	air separation
35	conduit
36	compressor
37	conduit
40	conduit
41	compressor
42	conduit
43	methanol synthesis

44	conduit
45	methanol distillation
46	conduit
T1	first partial stream
T2	second partial stream

Claims:

1. A process for producing a synthesis gas containing hydrogen and carbon monoxide from a starting gas containing hydrocarbons, wherein the starting gas is split up into a first partial stream (T1) and a second partial stream (T2), wherein the first partial stream (T1) is supplied to a steam reformer (13) in which it is catalytically converted together with steam to obtain a gas stream containing hydrogen and carbon oxides, wherein downstream the steam reformation the first partial stream (T1) is again combined with the second partial stream (T2), and wherein the combined gas stream is supplied to an autothermal reformer (32) in which the combined gas stream together with an oxygen-containing gas is autothermally reformed to a synthesis gas, **characterized in** that the first partial stream (T1) is guided directly into the steam reformer (13) and the second partial stream (T2) is guided through a pre-reformer (23) before passing through the autothermal reformer (32).

2. The process according to claim 1, **characterized in** that the hydrocarbons with two or more carbon atoms, which are contained in the partial stream (T2), are converted to at least 90 wt-% of carbon dioxide and methane in the pre-reformer (23).

3. The process according to claim 1 or 2, **characterized in** that the temperature of the combined gas stream lies between 660 and 800 °C.

4. The process according to any of the preceding claims, **characterized in** that the partial stream (T1) is supplied to the steam reformer (13) with a temperature between 500 and 600 °C and/or the partial stream (T2) is supplied to the pre-reformer (23) with a temperature between 400 and 500 °C.

5. The process according to any of the preceding claims, **characterized in** that the catalyst for the pre-reformer (23) has a nickel content between 2 and 20 wt-%.

6. The process according to any of the preceding claims, **characterized in** that the catalyst for the steam reformer (13) has a nickel content between 30 and 40 wt-%.

7. The process according to any of the preceding claims, **characterized in** that the reaction temperature in the pre-reformer (23) lies between 400 and 500 °C.

8. The process according to any of the preceding claims, **characterized in** that the reaction temperature in the steam reformer (13) lies between 600 and 800 °C.

9. The process according to any of the preceding claims, **characterized in** that the pre-reformer (23) is operated adiabatically.

10. The process according to any of the preceding claims, **characterized in** that the starting gas exits from the pre-reformer (23) with a temperature between 650 and 800 °C.

11. A plant for the production of a synthesis gas containing hydrogen and carbon monoxide from a starting gas containing hydrocarbons with a splitter (8) which splits up the starting gas into a first partial stream (T1) and a second partial stream (T2), with a steam reformer (13) in which the first partial stream (T1) is catalytically converted with steam to obtain a gas stream containing hydrogen and carbon oxides, and with an autothermal reformer (32) in which the first partial stream (T1) and the second partial stream (T2) are autothermally

reformed together with gas containing oxygen, **characterized in** that a conduit (10) leads from the splitter (8) into the steam reformer (13), via which the first partial stream (T1) is directly introduced into the steam reformer (13), and that between the splitter (8) and the autothermal reformer (32) a pre-reformer (23) is provided, through which the second partial stream (T2) is guided.

12. The plant according to claim 11, **characterized in** that in the conduit (10) upstream the steam reformer (13) and in the conduit (20) upstream the pre-reformer (23) at least one heat exchanger (12, 22) each is provided.

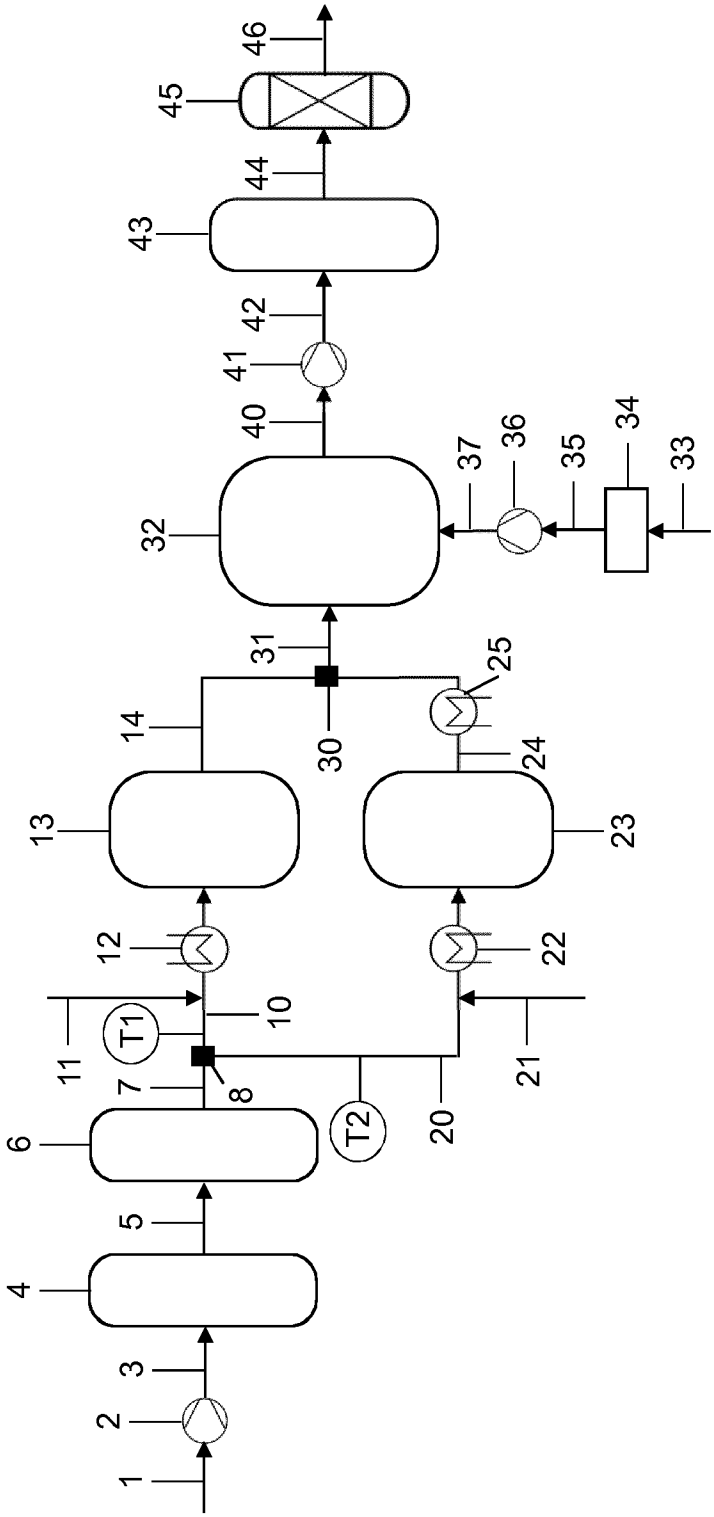

1
2
3
4
5
6
7
8
10
11
12
13
14
20
21
22
23
24
25
30
31
32
33
34
35
36
37
40
41
42
43
44
45
46
T1
T2

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/052646

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38
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)
C01B

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.
X	DE 10 2008 039014 A1 (UHDE GMBH [DE]) 25 February 2010 (2010-02-25) paragraph [0068] figure 24 -----	1-11
A	DE 10 2006 023248 A1 (LURGI AG [DE] LURGI GMBH [DE]) 22 November 2007 (2007-11-22) cited in the application paragraphs [0024], [0025] -----	1-12
A	EP 1 616 838 A2 (AIR PROD & CHEM [US]) 18 January 2006 (2006-01-18) the whole document -----	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 April 2014	14/04/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Harf-Bapin, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/052646

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102008039014 A1	25-02-2010	DE 102008039014 A1	25-02-2010
		WO 2010020358 A2	25-02-2010
DE 102006023248 A1	22-11-2007	CN 101448731 A	03-06-2009
		DE 102006023248 A1	22-11-2007
		EP 2021274 A1	11-02-2009
		US 2009105356 A1	23-04-2009
		WO 2007134727 A1	29-11-2007
EP 1616838 A2	18-01-2006	CA 2511406 A1	08-01-2006
		CN 1718536 A	11-01-2006
		EP 1616838 A2	18-01-2006
		ES 2404038 T3	23-05-2013
		US 2006008413 A1	12-01-2006
		US 2008300130 A1	04-12-2008