



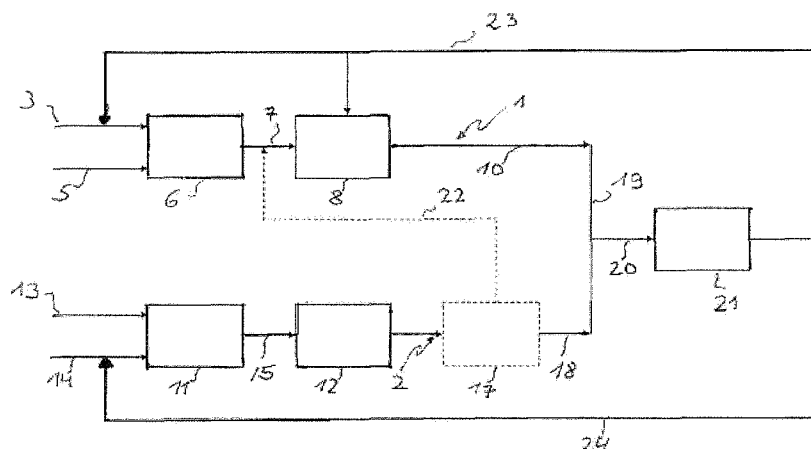
- (51) International Patent Classification:
C01B 3/38 (2006.01)
- (21) International Application Number:
PCT/EP2012/061631
- (22) International Filing Date:
19 June 2012 (19.06.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
PA 2011 00567 25 July 2011 (25.07.2011) DK
- (71) Applicant (for all designated States except US):
HALDOR TOPSØE A/S [DK/DK]; Nymøllevej 55, DK-2800 Kgs. Lyngby (DK).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): DAHL, Juul Per [DK/DK]; Krumningen 16, DK-2950 Vedbæk (DK).
- (74) Common Representative: HALDOR TOPSØE A/S; Nymøllevej 55, DK-2800 Kgs. Lyngby (DK).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, 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, 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).

Published:
— with international search report (Art. 21(3))

(54) Title: PROCESS FOR PRODUCTION OF SYNTHESIS GAS

Fig. 1



(57) Abstract: The invention relates to a flexible process for the production of synthesis gas from a hydrocarbon feedstock and which is particularly suitable for large methanol, ammonia and liquid hydrocarbon plants. The synthesis gas is produced in two single line steam reforming steps.

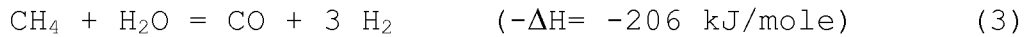
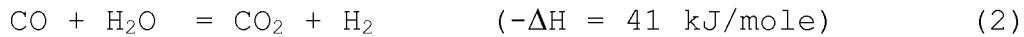
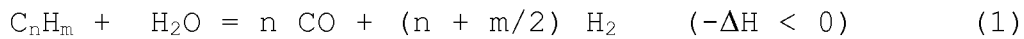
Title: Process for Production of Synthesis Gas

This invention relates to a process for the conversion of hydrocarbon feed to synthesis gas which can be further converted and/or purified as required for production of hydrogen, carbon monoxide, mixtures of hydrogen and carbon monoxide, as well as for the production of methanol, dimethyl ether (DME), and liquid hydrocarbons. In particular the invention relates to a combined reforming process for the preparation of synthesis gas suitable for conversion of a hydrocarbon feed stock to such products in plants of large capacity capable of converting hydrocarbon feed to more than 8000 metric tons per day of such products.

The synthesis gas section is the most expensive section of a plant for conversion of hydrocarbon feed to end products, both in terms of energy requirements and capital costs. Therefore, major efforts have been focusing on finding alternative process schemes for synthesis gas production which are less expensive and/or more energy efficient than hitherto known.

Synthesis gas technology includes steam reforming (tubular or primary reforming) and pure oxygen autothermal reforming (ATR), enriched air ATR and air ATR (secondary reforming). Steam reforming can be divided into adiabatic prereforming (APR), tubular reforming with external firing (SMR) and heat exchange reforming (HTER).

In the steam reforming process, synthesis gas is produced from hydrocarbon feedstock by reactions (1) - (3):



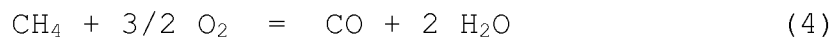
5 During primary reforming, the reactions 1-3 are carried out
in an externally heated reactor, hereinafter referred as a
primary reformer (SMR). The feed to the primary reformer
may be desulphurised hydrocarbon feed mixed with steam or
the partly converted product gas from a previous prereform-
10 ing step. The primary reformer is often a fired tubular re-
former consisting of catalyst filled tubes placed in a fur-
nace heated by one or several burners and which operates at
conditions where the outlet temperature from the catalyst
filled tubes is relatively high, usually in the range 650
15 to 950°C.

Heat exchange reformers used in such concepts are also
known as heat exchange reformers or gas heated reformers.

20 Autothermal reforming (ATR) is a technology used for the
production of synthesis gas in which the conversion of a
hydrocarbon feedstock or the conversion of a partly con-
verted gas from a prereforming step into synthesis gas is
completed in a single reactor by the combination of partial
25 combustion and adiabatic steam reforming. Combustion of hy-
drocarbon feed is carried out with substoichiometric
amounts of air, enriched air or oxygen by flame reactions
in a burner combustion zone. Steam reforming of the par-
tially combusted hydrocarbon feedstock is subsequently con-
30 ducted in a fixed bed of steam reforming catalyst.

Secondary reforming is a process in which partly converted (partly reformed) feed from a primary reforming step is further converted by the combination of partial combustion and adiabatic steam reforming. The secondary reformer in ammonia plants is usually air-blown while in methanol, DME and hydrocarbon synthesis plants it is oxygen blown.

In autothermal reforming and secondary reforming the steam reforming reactions 1-3 are supplemented by partial combustion, which may be represented by reaction (4):



It is conventional to produce synthesis gas by first passing a hydrocarbon feedstock mixed with steam through a steam reforming step, which comprises passing the feedstock through a prereformer, then a primary reformer, and finally through a secondary reformer fired with air, enriched air or oxygen. This combination of steam reforming followed by secondary reforming is often referred to as two-step reforming and is particularly suitable for the preparation of synthesis gas suitable for methanol, dimethyl ether and ammonia production. By controlling the amount of reforming occurring prior to the secondary reformer, a synthesis gas having the correct stoichiometry for methanol synthesis or a synthesis gas having the correct hydrogen-to-nitrogen ratio for ammonia synthesis or any other application can be prepared.

During the prereforming, reactions 1-3 are carried out in adiabatic reactors, also called adiabatic prereformers (APR), at relatively low temperatures, usually 350° to

650°C. An adiabatic reactor is a reactor in which no heat is transferred to or from the reacting stream (except for heat loss to the surroundings).

5 Frequently the above reforming techniques are combined either in series or in parallel.

Typical reforming combinations are:

- 10 - SMR
- SMR, Secondary Reforming
- APR, SMR
- APR, SMR, Secondary Reforming
- ATR
- 15 - APR, ATR

All the above configurations can be paired with heat exchange reforming (HTER) in parallel as well as in series.

20 It is also known to produce a synthesis gas by splitting a hydrocarbon feed stream into separate streams prior to reforming in order to reduce the capacity required in the primary reformer and to reduce the overall steam-to-carbon ratio in the reforming process, thereby reducing the mass
25 flow through the plant and consequently the size of equipment.

US patent 6,444,712 discloses a method for the production of methanol and hydrocarbons from synthesis gas being obtained from two parallel single lines steam reforming. In
30 one single line, a methane containing gas is subjected to primary steam reforming in an SMR and the other single

line, a methane containing gas is directed a partial oxidation reformer. The synthesis gas produced in both single lines is introduced into the methanol synthesis step.

5 The partial oxidation reactor may be an ATR. US 6,444,712 is silent about the steam to carbon ratio in the feed gas to the parallel single lines steam reforming.

10 The required steam-to-carbon ratio (S/C-ratio), defined as the molar ratio between the total amount of steam added to the process in the steam reforming step and the carbon contained in the hydrocarbon feed, depends on the particular steam reforming technique, as further explained in the following description.

15 The steam required for the process can be added as one stream before a prereforming step and another supplementary stream after the prereforming step; if no prereforming step is present the steam is added before the steam reforming step.

20

The optimum synthesis gas composition depends on the product to be produced. One way of characterising a synthesis gas composition is by means of the molar ratio of $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$ (M1) and the molar ratio of H_2/CO (M2).

25

The amount of steam added to the carbon feed to be reformed is very important because it has an impact on M1 and M2. More steam increases the value of both. Table 1 lists typical values/ranges of steam-to-carbon ratio, M1, M2 and approximate single line synthesis gas production capacity for
30 various reforming reactors.

Table 1

Reforming reactor	Steam to Carbon S/C	M1	M2	Approx Max Capacity in MTPD, Single line
SMR	>1,4	2,5-3,0	2,7-4,6	3000
ATR	>0,4	1,4-1,8	0,7-1,4	7500
SMR - ATR	>1,4	1,9-2,3		7500

Typically required M1 and M2 in synthesis gas for the optimum production of methanol, hydrocarbons and gasoline are listed in Table 2

Table 2

	M1	M2
Methanol	1,9-2,3	
Fischer Tropsch		0,8-1.1
Gasoline		0,8-1,1

10

The maximum capacity in a plant is related to the amount of product such as methanol, gasoline, and hydrocarbons which can be produced in a process scheme for synthesis gas production consuming a given amount of oxygen and usually involving a steam reforming step with a given transferred duty. In some cases the maximum capacity may be determined by the maximum allowable pressure drop in the adiabatic oxidative reactor (ATR or secondary reformer) of the maximum practical size. The pressure drop in a given ATR reactor or secondary reformer depends on the total volumetric

15

20

flow of product gas from the adiabatic oxidative reactor, i.e. its exit flow, so that the maximum achievable capacity with good approximation is defined by a maximum allowable volumetric flow of wet product gas from the adiabatic oxidative reactor.

Usually, one of either the size of the steam reformers, the supply of oxygen from an air separation unit to the ATR reactor or the exit flow of the ATR represents the bottleneck for the capacity in terms of for instance methanol production from the produced synthesis gas. It is desirable to obtain an increased plant capacity for the same steam reformer size or duty when for instance the duty of the steam reformer represents the bottleneck for the capacity. Similarly, it is desirable to obtain an increased plant capacity for the same exit flow from the adiabatic oxidative reactor when the duty of the steam represents the bottleneck for the capacity.

Furthermore, low steam-to-carbon ratios increase the possible maximum size and decrease the investment and operating costs. An SMR requires a steam-to-carbon ratio above 1.4 whereas an ATR can operate at steam to carbon ratios down to 0.4. This means that for capacities larger than the achievable single line capacity it is an advantage to maintain a single line design and thereby to achieve optimum synthesis gas composition for example for methanol production by mixing synthesis gas from individual optimized reforming sections.

30

Thus, the main object of this invention is to provide a process for the preparation of synthesis gas producing a

maximum amount of synthesis gas with a specific M1 and M2, said production exceeding the maximum production capacity of a single line process as defined in Table 1.

5 Accordingly, the invention provides a process for the production of synthesis gas in two single line steam reforming steps comprising:

(a) forming a first hydrocarbon stream by desulphurising a
10 hydrocarbon feedstock and introducing an amount of steam into the desulphurized first hydrocarbon stream to provide a steam-to-carbon ratio of between 1.4 and 1.8;

(b) forming a second hydrocarbon stream by desulphurising a
15 hydrocarbon feedstock and introducing an amount of steam into the desulphurized second hydrocarbon stream to provide a steam-to-carbon ratio of between 0.4 and 0.8;

(c) passing the first hydrocarbon stream through a first
20 single line steam reforming step comprising primary reforming to obtain a first synthesis gas product comprising hydrogen, carbon monoxide and carbon dioxide;

(d) passing the second hydrocarbon stream through a second
25 single line steam reforming step comprising an autothermal reforming to obtain a second synthesis gas product comprising hydrogen, carbon monoxide and carbon dioxide; and

(e) mixing the first and second synthesis gas product in
30 an amount to provide a module M1 of between 1.4 and 3.0 and a module M2 of between 0.7 and 4.6, where

M1 is the molar ratio of $(\text{H}_2-\text{CO}_2)/(\text{CO}+\text{CO}_2)$ and

M2 is the molar ratio of H_2/CO .

As used herein the term steam-to-carbon ratio (S/C) is defined by the molar ratio between the amount of steam added to the process gas in a given single line of steam reforming and the carbon contained in the hydrocarbon feed to said reforming step.

By the invention, process parameters such as steam-to-carbon ratio, amount of the hydrocarbon feedstock, reformer duty in a heated steam reformer, and amount of oxygen added in the adiabatic oxidative reactor for the conversion of the second hydrocarbons stream into synthesis gas, can be expediently adjusted so as to obtain a maximum amount of combined synthesis gas from the two single line reforming steps with predetermined $\text{H}_2/\text{CO}/\text{CO}_2$ molar ratios which are suitable for the production of large amounts (several thousand metric tons per day (MTPD)) of products in any given downstream application, such as methanol and/or DME synthesis, ammonia synthesis and synthesis of liquid hydrocarbons, e.g. gasoline. Thus, it is possible to optimize the operating conditions in the primary reforming step of the first hydrocarbon stream and in the autothermal reforming step of the second hydrocarbon stream individually, in particular by adjusting the optimum steam to carbon ratio individually in the first and second hydrocarbon stream.

In one particular embodiment of the invention, the process further comprises prereforming of the first and/or second hydrocarbon stream. Preferably the prereforming is conducted adiabatically.

The prereforming step provides the possibility of heating the first and/or the second stream to higher temperatures than in processes operating without the prereforming step.

5

The reforming in steps (c) and (d) may be performed by passing the hydrocarbon streams through a series of one or more reforming steps in each single line. The steam reforming may thus be conducted in one or more heated steam reforming stages in series and/or in one or more autothermal reforming stages in series, respectively.

10

In a further embodiment the heat required for the reforming in step (c) is preferably provided by indirect heat exchange with flue gas from the SMR and/or produced synthesis gas withdrawn from the ATR in step (d).

15

In some application it is advantageous to further reform the synthesis gas from the primary reforming in step (c) by passing the primary reformed gas through an auto thermal reforming step.

20

Thus, in yet a further embodiment of the invention, the steam reforming in step (c) further comprises autothermal steam reforming downstream the primary reforming.

25

By the invention it is possible to increase the CO/CO₂ molar ratio in the synthesis gas by removing at least part of the CO₂ from the synthesis gas leaving the reforming step (d) and directing at least part of this CO₂ to the inlet of the reforming step (c). Synthesis gas becomes more reactive at increased CO/CO₂ molar ratios. A more reactive syn-

30

thesis gas reduces the size of the synthesis reactors/units, such as for example a methanol synthesis reactor. Furthermore this improved synthesis gas is by this method obtained without loss of an overall carbon efficiency

Thus, in yet a further embodiment of the invention at least part of the carbon dioxide is removed from the second synthesis gas product and directed to the heated primary reforming in step in step (c).

By the invention it is also possible to achieve a high degree of flexibility in terms of the composition of the synthesis gas being prepared for a particular application, in particular for very large plants, i.e. plants capable of producing several thousand MTPD, such as 10000 MTPD or more of methanol, ammonia, DME (dimethyl ether) or liquid hydrocarbons or any combination of these products. Synthesis gas for the production of methanol is also suitable for the production of liquid hydrocarbons by Fischer-Tropsch synthesis, while methanol, DME or methanol/DME mixtures are suitable oxygenates for the production of liquid hydrocarbons such as gasoline according to for instance integrated gasoline synthesis described in US Patent 4,481,305.

Therefore the invention also encompasses a process according to claim 1 further comprising converting the synthesis gas from step (e) into ammonia, methanol, DME, liquid hydrocarbons, or combinations thereof.

Catalysts employed in the reforming stage of each single line and for converting the resulting produced synthesis

gas into ammonia, methanol, DME and liquid hydrocarbons are per se known in the art and are not a part of this invention.

5 The invention is described in greater detail in the following by reference to the drawings, in which Fig.1 is a simplified flow sheet of a particular embodiment of the invention for the production of synthesis gas employed in the preparation of methanol.

10

Referring to Fig.1, synthesis gas is produced according to two single lines 1 and 2, arranged in parallel. Single line 1 includes in series an adiabatic prereformer 6 and a primary reformer 8. Desulphurized hydrocarbon feed stock is introduced into the single line 1 together with steam 5. The amount of steam is adjusted to provide an S/C ratio of 1.8 in the steam hydrocarbon mixture before being passed to an adiabatic prereformer 6. Prereformed gas is directed via line 7 to a primary reformer 8. The operating conditions in reformer 8 are adjusted to provide a final synthesis gas 10 according to single line 1 with a module M1 of 3.0.

The single line 2 includes an adiabatic prereformer 11 and an autothermal reformer 12. Line 2 is fed with hydrocarbon feed stock 13 and steam 14. The amount of steam passed into single line 2 is adjusted to provide an S/C ratio of 0.6. The steam hydrocarbon mixture is prereformed in reformer 11, and the prereformed gas 15 is directed to an autothermal reactor 12. Reactor 12 is operated with pure oxygen (>99.5). The operation conditions of reactor 12 are adjusted to result in module M1 of 1.9 in the final synthesis gas 18 according to single line 2 after an optional removal

30

of carbon dioxide in the reformed gas by means of CO₂ wash
17.

The ratio between the amounts of hydrocarbon feed 3 and 13
5 is adjusted to result in a module M1 in the combined syn-
thesis gas of 2.1.

The synthesis gases 10 and 18 are mixed in a synthesis gas
header 19 and the combined synthesis gas 20 with a module
10 M1 of 2.1 is passed to methanol synthesis 21.

Optionally, carbon dioxide resulting from the CO₂ removal
in the stripper 17 is passed via line 22 to the prereformed
gas in line 7 of the single line 1 when higher amounts of
15 carbon monoxide in the primary reformed gas 10 are re-
quired.

A further option is to recycle part of the tail gas from
the methanol reactor 21 consisting mainly of unconverted
20 synthesis gas to single line 1 via line 23 and/or to single
line 22 via line 24, as shown in Fig. 1.

As an example the optimum design for a 10000 MTPD MeOH
plant is a synthesis gas section consisting of a single
25 line with APR-SMR units corresponding to 2500 MTPD and a
single line with APR-ATR units corresponding to 7500 MTPD.
This solution is compared with two APR, SMR, ATR units (two
step reforming) each unit presenting a capacity of 5000
MTPD. The calculations show that for similar/identical con-
30 sumption figures a considerable saving in investment costs
can be achieved by the invention.

CLAIMS

1. Process for the production of synthesis gas in two single line steam reforming steps comprising:

5

(a) forming a first hydrocarbon stream by desulphurising a hydrocarbon feedstock and introducing an amount of steam into the desulphurized first hydrocarbon stream to provide a steam-to-carbon molar ratio of between 1.4 and 1.8;

10

(b) forming a second hydrocarbon stream by desulphurising a hydrocarbon feedstock and introducing an amount of steam into the desulphurized second hydrocarbon stream to provide a steam-to-carbon molar ratio of between 0.4 and 0.8;

15

(c) passing the first hydrocarbon stream through a first single line steam reforming step comprising heated primary reforming to obtain a first synthesis gas product comprising hydrogen, carbon monoxide and carbon dioxide;

20

(d) passing the second hydrocarbon stream through a second single line steam reforming step comprising an autothermal reforming to obtain a second synthesis gas product comprising hydrogen, carbon monoxide and carbon dioxide; and

25

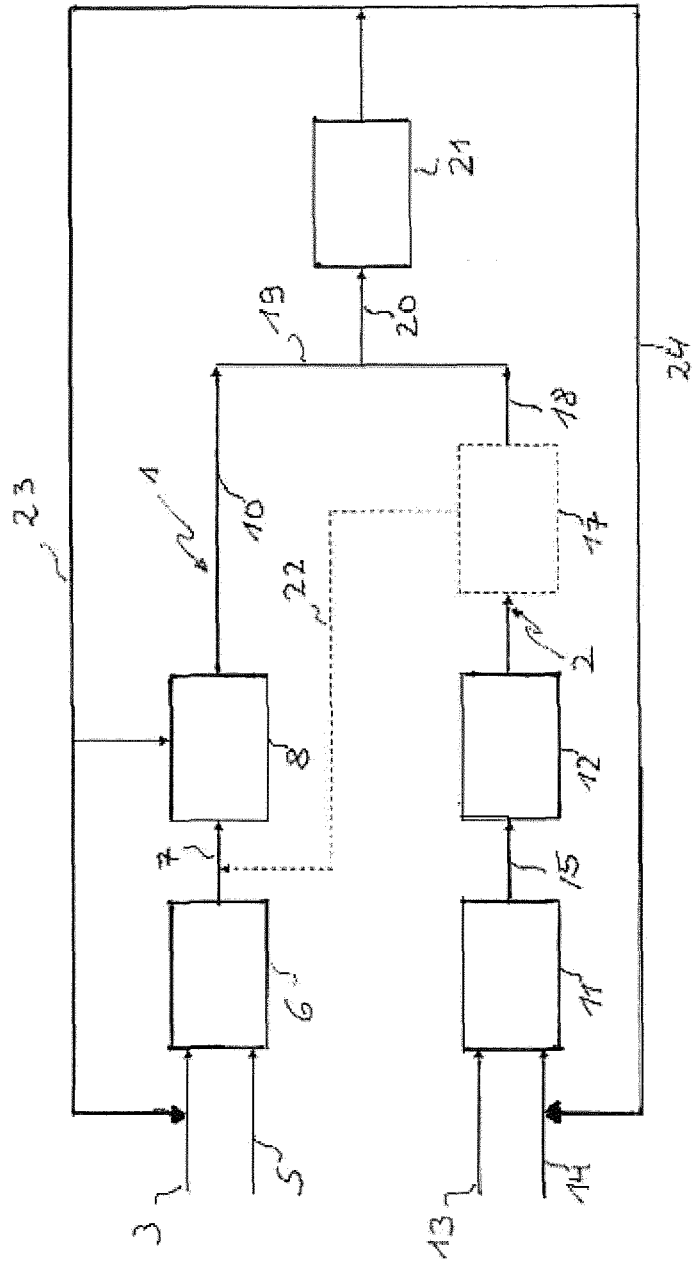
(e) mixing the first and second synthesis gas product in an amount to provide in the mixed synthesis gas a module M1 of between 1.4 and 3.0 and/or a module M2 of between 0.7 and 4.6, where

30

M1 is the molar ratio of $(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2)$; and
M2 is the molar ratio of H_2 / CO .

2. Process according to claim 1 wherein step (a) and/or step (b) further comprises adiabatic pre-reforming.
- 5 3. Process according to claims 1 or 2, wherein the primary reforming in step (c) is performed in on or more tubular steam reformers connected in series.
4. Process according to anyone of claims 1 to 3, wherein
10 the autothermal reforming in step (d) is performed in one or more autothermal reformers connected in series.
5. Process according to anyone of claims 1 to 4, wherein
15 at least part of the heat required for the reforming in step (c) is provided by indirect heat exchange with second synthesis gas product withdrawn from the autothermal reforming in step (d).
6. Process according to anyone of claims 1 to 5, wherein
20 the steam reforming in step (c) further comprises autothermal steam reforming downstream the primary reforming.
7. Process according to anyone of claims 1 to 6, further
25 comprising a step of removing at least part of the carbon dioxide from the second synthesis gas product and directing the removed carbon dioxide to the heated primary reforming in step (c).
8. Use of a process according to anyone of the preceding
30 claims for synthesis of ammonia, methanol, DME, liquid hydrocarbons, or combinations thereof.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061631

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	US 2007/004809 A1 (LATTNER JAMES R [US] ET AL) 4 January 2007 (2007-01-04) claims	1-8
X	WO 2006/117499 A1 (QUARTEY-PAPAFIO ALEXANDER H [GB]) 9 November 2006 (2006-11-09) paragraph [0039] - paragraph [0051]; figure 3	1-8
X	EP 0 999 178 A1 (AMMONIA CASALE SA [CH]) 10 May 2000 (2000-05-10) claims	1-8
X	EP 0 522 744 A2 (ICI PLC [GB]) 13 January 1993 (1993-01-13) page 3, line 4 - line 20; figures 1-4	1-8
	-/--	

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 24 July 2012	Date of mailing of the international search report 01/08/2012
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 Van der Poel, Wim

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061631

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 403 216 A1 (TOPSOE HALDOR AS [DK]) 31 March 2004 (2004-03-31) figures -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/061631

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007004809	A1	04-01-2007	US 2007004809 A1
			WO 2007005126 A1

WO 2006117499	A1	09-11-2006	NONE

EP 0999178	A1	10-05-2000	AU 5713099 A
			BR 9917439 A
			CA 2287743 A1
			CN 1253114 A
			DE 69835357 T2
			EP 0999178 A1
			ID 25973 A
			US 6207078 B1
			US 2001006615 A1

EP 0522744	A2	13-01-1993	AT 156778 T
			AU 649548 B2
			AU 1864892 A
			CA 2073526 A1
			DE 69221556 D1
			DE 69221556 T2
			EP 0522744 A2
			IN 182302 A1
			NO 922696 A
			NZ 243382 A
			US 5252609 A

EP 1403216	A1	31-03-2004	AT 502894 T
			AU 2003248393 A1
			CA 2442770 A1
			CN 1496954 A
			EP 1403216 A1
			JP 4351010 B2
			JP 2004269343 A
			KR 20040027448 A
			RU 2345948 C2
			US 2004063798 A1
