



(51) International Patent Classification:

C01B 3/38 (2006.01) **C01B 31/26** (2006.01)
C01B 17/50 (2006.01)

(21) International Application Number:

PCT/EP2009/001918

(22) International Filing Date:

13 March 2009 (13.03.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): **ENI S.p.A.** [IT/IT]; Piazzale E. Mattei, 1, I-00144 Roma (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BELLUSSI, Giuseppe** [IT/IT]; Via E. Millo 14, I-29100 Piacenza (IT). **DE ANGELIS, Alberto** [IT/IT]; Via F. Ili Cairoli, 16, I-20025 Legnano (Milano) (IT). **POLLESEL, Paolo** [IT/IT]; Via Dossetti 11/D, I-20097 San Donato Milanese (Milano) (IT). **PEREGO, Carlo** [IT/IT]; Via S. Cornelio e Cipriano 15/E, I-20040 Carnate (Milano) (IT).

(74) Agent: **DE GREGORI, Antonella**; Barzano' & Zanardo Milano S.p.A., Via Borgonuovo 10, I-20121 Milan, Italie (IT).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, 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 THE ABATEMENT OF HYDROGEN SULPHIDE FROM COMPOSITIONS CONTAINING IT WITH SIMULTANEOUS PRODUCTION OF HYDROGEN

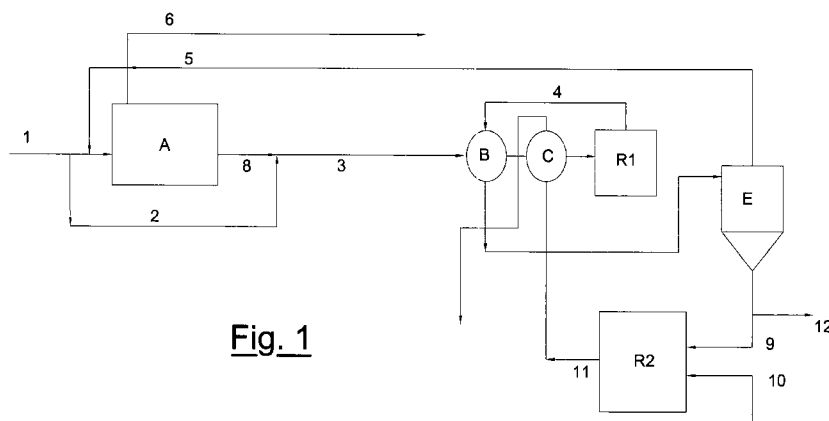


Fig. 1

(57) Abstract: Process for the abatement of hydrogen sulphide from compositions containing it with the contemporaneous production of hydrogen, comprising: a. treating hydrogen sulphide with methane (reforming) according to the endothermic reaction: $2 \text{H}_2\text{S} + \text{CH}_4 = \text{CS}_2 + 4\text{H}_2$ (1) b. cooling the reaction products and separating the carbon disulphide (CS_2); c. burning the carbon disulphide; d. feeding at least an aliquot of the hot gases from the combustion of carbon disulphide to the reforming step, as a heat source for maintaining the endothermic reaction (1). e. disposing of the cooled gases from the combustion of carbon disulphide.

5

PROCESS FOR THE ABATEMENT OF HYDROGEN SULPHIDE FROM
COMPOSITIONS CONTAINING IT WITH SIMULTANEOUS PRODUCTION OF
HYDROGEN

The present invention relates to a process for the
10 abatement of hydrogen sulphide from compositions containing
it with the contemporaneous production of hydrogen.

More specifically, the present invention relates to a
process for the abatement/sweetening of hydrogen sulphide
contained in gaseous streams.

15 Hydrogen sulphide is a noxious gas present in many re-
fineries as by-product of hydrodesulphuration installa-
tions, and in many oil fields as a blend with natural gas
and light hydrocarbons (gas sour) or as a blend with natu-
ral gas and carbon dioxide (acidic gases).

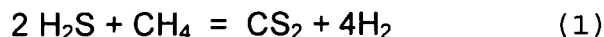
20 Hydrogen sulphide is normally separated from gases by
means of absorption with an amine solution and is then sent
to a Claus plant in which it is transformed to sulphur.

By operating in this way, the hydrogen present in the
molecule of hydrogen sulphide is burned to produce water,
25 whereas the sulphur in the H₂S molecule is converted into

elemental sulphur.

Hydrogen is a raw material which is highly requested in refineries for all hydrotreatment processes, such as hydrocracking and hydrodesulphuration, it would consequently
5 be greatly desirable to be able to obtain it from a source at zero value, such as hydrogen sulphide.

A method which allows hydrogen to be obtained from H₂S is methane reforming according to the reaction:



10 This reaction can be carried out with high conversions only at high temperatures (higher than 900°C, for example) and it is highly endothermic ($\Delta\text{H}_{298} = 232 \text{ kJ/mole}$), energy must therefore be provided from the outside, by burning a fuel, such as, for example, the same acid methane for H₂S,
15 with a considerable increase in the production costs.

Furthermore, the CS₂ thus produced has a limited market, which is continuously decreasing due to the progressive elimination from the market of Freon, which represented one of the derivatives with highest added margin.

20 The Applicant has now found, and this represents an object of the present invention, that it is possible to abate hydrogen sulphide from compositions containing it, with the contemporaneous production of hydrogen, by means of an integrated cycle wherein the CS₂ produced by the reforming reaction between methane and H₂S is burned to pro-
25

duce CO₂ and SO₂, thus obtaining a blend which can be either advantageously used for the synthesis of sulphuric acid or it can be disposed of by means of traditional methods, for example by injecting it into the subsoil. Furthermore, by exploiting the large quantity of reaction heat developed during the combustion of CS₂ ($\Delta H_{298} = -1032$ kJ/mole) the previous endothermic reaction of H₂S reforming with methane can be sustained without burning any valuable fuel.

An object of the present invention therefore relates to a process for the abatement of hydrogen sulphide from compositions containing it with the contemporaneous production of hydrogen, comprising:

- a. feeding a blend comprising methane and hydrogen sulphide to a reforming reactor operating at a temperature ranging from 900 to 1,500°C and at atmospheric pressure or slightly lower, for example between 0.08 and 0.1 MPa, to produce a blend essentially consisting of carbon disulphide (CS₂) and hydrogen (H₂);
- b. cooling the reaction products and separating the carbon disulphide from the remaining reaction blend containing hydrogen;
- c. burning the carbon sulphide with a gas containing oxygen to produce a gaseous blend, essentially consisting of CO₂ and SO₂, at a high temperature;

- d. feeding at least a part of the hot gases of the carbon disulphide combustion to the reforming step, as a heat source for maintaining the endothermic reaction of step (a); and
- 5 e. using the combustion gases of carbon disulphide, coming from step (d), as intermediate products for downstream chemical syntheses or disposing of them by injection into suitable geological structures.

According to the present invention, the reforming reaction of methane/H₂S preferably takes place at a temperature ranging from 900 to 1,300°C. This type of reaction is known in literature and is described, for example, in the article of S. K. Megalofonos and N. G. Papayannakos in "International Journal of Hydrogen Energy", vol. 16(5) 1991, pages 10 319-327, and can also be effected in the presence of a catalyst. Typical examples of catalysts are metal sulphides of Group VIB, VIIB and VIIIB of the periodic table of elements and, among these, sulphides of chromium, molybdenum, tungsten, iron, cobalt and nickel are particularly preferred. 15 20

In general, the blends comprising methane and hydrogen sulphide are gaseous streams from refinery plants or they are streams of natural gas from production fields, or gas streams associated with oilfields. These streams can include other inert/acid gases such as nitrogen or carbon di- 25

oxide. They are preferably gaseous streams in which the H_2S concentration ranges from 1 to 65% moles with respect to the total.

When the H_2S concentration in the gaseous stream containing methane is low, or, in any case, is not such as to satisfy the conditions of the reforming reaction, the stream is preferably treated in an absorption plant of hydrogen sulphide with amines, in order to concentrate and recover it. The hydrogen sulphide stripped from the absorbing liquid, can be recombined with a fraction of the gaseous stream containing it so as to have ratios between H_2S and CH_4 which allow the reforming reaction to be profitably effected.

The reforming reaction preferably takes place with $\text{CH}_4/\text{H}_2\text{S}$ molar ratios higher than the stoichiometric value of 0.5, for example between 0.51 and 10, so as to reduce the non-reacted hydrogen sulphide concentration in the reaction products, to negligible values.

At the end of the reforming, the reaction products are cooled to an optimal temperature for the subsequent operations, for example to temperatures lower than 50°C , in order to recover carbon sulphide, which is liquid at those temperatures, from the gaseous phase essentially consisting of hydrogen, methane and/or residual H_2S and possible reaction by-products. The gaseous phase can then be treated

with conventional methods, for example by means of the selective adsorption technology, of the PSA type, or membrane treatment, for the recovery of hydrogen.

The cooling phase is preferably effected in heat exchangers in which the cooling liquid is water which can be transformed into vapour at a temperature of 100-150°C and a pressure of 0.2-10 MPa. The vapour can be used for producing electric energy or as a heat source destined for the running of other plants. Alternatively, before cooling in the heat exchanger, the reaction products can pre-heat the reagents which are to be fed to the reforming reactor.

The carbon sulphide, recovered in the liquid state, is burned in a specific reactor, with air or air enriched in oxygen as comburent.

The combustion gases, which leave the combustion reactor at a temperature of 1,000-2,500 °C are partially or totally fed to a further heat exchanger system to heat the reagents, possibly pre-heated, to the right temperature before entering the reforming reactor.

In this way, from the integrated cycle described, object of the present invention, the production of hydrogen can be obtained from a stream containing hydrogen sulphide without having to use any external high-quality fuel, and a stream, containing SO₂, is also obtained as by-product, which can be advantageously used as raw material for chemi-

cal syntheses, such as, for example, the production of sulphuric acid. Alternatively, if convenient, the stream containing SO_2 can be injected into suitable geological structures.

5 If the starting mix is natural acidic gas for H_2S , the considerable quantity of heat produced by the combustion of CS_2 can also be used for sustaining the separation of methane from H_2S by means of the conventional amine process, if the quantity of H_2S present in the gaseous stream is con-
10 siderably lower than the $\text{H}_2\text{S}/\text{CH}_4$ molar ratio required by the reforming reaction.

An alternative embodiment of the process object of the present invention, again if the starting material is natural gas, envisages that only a portion of the CS_2 produced
15 be burned as energy source, whereas the remaining portion is separated and destined for commercialization.

The balance between the aliquot of CS_2 burned and that separated and sold, depends on the quantity of heat to be produced for sustaining the endothermic reforming reaction
20 of methane with H_2S . The sufficient quantity of CS_2 to be destined for combustion for sustaining the methane reforming with H_2S is at least equal to 55% by weight of the total CS_2 produced. The remaining part of CS_2 can, according to necessity, be separated and sold or burned to provide
25 thermal energy for also sustaining other equipment of the

process, such as for example the amine plant, or it can be used for producing high pressure vapour which can be used in this or other plants.

Another innovative aspect of the process object of the present invention is represented by the fact that the sulphur present in the H_2S molecule is transformed into SO_2 , which, in turn, can be transformed, through reactions and processes which are well-known in literature, into sulphuric acid, for example, requested by the chemical industry, instead of into elemental sulphur as in the conventional Claus process.

Elemental sulphur, in fact, has considerable environmental problems relating to its storage and many nations in which there are oil fields impose heavy economical sanctions for sulphur storage.

If, on the contrary, sulphur is transformed into sulphuric acid, an easily transportable liquid product is obtained which can be commercialized as such.

The process for the abatement of hydrogen sulphide from compositions containing it, with the contemporaneous production of hydrogen, object of the present invention, can be better understood with reference to the enclosed figure which represents an illustrative but non-limiting embodiment.

With reference to the figure, A is a conventional amine

plant for the sweetening of acid gas, B is a thermal recovery heat exchanger, C is a heat exchanger system useful for providing the energy necessary for the reforming, R1 is the methane/H₂S reforming reactor and can be, for example, a
5 fixed- or fluid-bed catalytic reactor, E is a condensation and collection system of the CS₂ produced in the reactor R1, R2 is the combustion reactor of CS₂.

A stream of acid gas (1) is provided, essentially consisting of methane and a fraction of H₂S equal, for example, to 10% molar. The stream is fed to an amine treatment
10 plant in order to concentrate the H₂S fraction. More specifically, an aliquot (2) of the main stream by-passes the amine plant A, whereas the remaining part is processed in this plant for the recovery of hydrogen sulphide containing
15 (8). This process step is optional as its existence is linked to whether or not the H₂S concentration in the feeding stream (1) is such as to satisfy the conditions of the CH₄/H₂S reforming reaction.

The stream (2) is recombined with hydrogen sulphide (8)
20 so as to form a stream (3) essentially consisting of methane and H₂S with the correct molar ratios for the reforming reaction.

The stream (3) is pre-heated in B, brought to the reforming reaction temperature in C and then fed to the reactor R1.
25

The hot reaction products (4) are recovered from the reactor R1, at a temperature of about 900-1,500 °C, for example. These hot gases are fed to B in order to pre-heat the reagents and are then fed to the condenser E, in which
5 the carbon sulphide CS₂, in the liquid state, stream (9), is separated from the gaseous phase essentially consisting of H₂, non-reacted H₂S and methane, stream (5). An aliquot of the carbon sulphide produced, stream (12), can be diverted from the cycle, object of the present invention, and
10 can be destined for other purposes.

The carbon sulphide (9) and comburent air (10) are fed to the combustion reactor R2. The combustion gases, stream (11), comprising CO₂ and SO₂, leave the reactor at a temperature of about 1,000-2,500°C and are fed directly to the
15 heat exchanger C, where the reagent gases (CH₄ and H₂S) are heated to a temperature of about 900-1,500°C or slightly higher. The stream of heated reagent gases (13) is fed to the reactor R1, in which the catalyst is contained, consisting, for example, of one or more metal sulphide(s) of
20 groups VIB, VIIB and VIIIB of the periodic table of elements. Sulphides of chromium, tungsten, molybdenum, iron, cobalt and nickel, used alone or combined, are particularly preferred among these metal sulphides. The temperature inside R1 is uniformly maintained at about 900-1,500°C.

25 After heating the reagents of the reforming reaction to

the reaction temperature, the combustion gases of carbon sulphide can be further cooled, in specific equipment not shown in the scheme of the enclosed figure and then used for chemical processes, for example, the synthesis of sulphuric acid, or they can be disposed of by injecting them
5 into the ground or into deep seawater.

The products of the reforming reaction which, after cooling in E, are in gaseous phase, stream (5), essentially consist of methane (the reaction excess) and hydrogen. As
10 they can still entrain considerable traces of non-reacted hydrogen sulphide, they are carefully fed to the plant A, for the recovery of these traces. In the end, the stream (6), essentially consisting of methane and hydrogen, is discharged from the plant A.

15 An illustrative and non-limiting example is provided hereunder for a better understanding of the present invention and for its embodiment.

EXAMPLE

A stream of 1,100 Nm³/h of a methane + hydrogen sulphide blend, consisting of 1,000 Nm³/h of methane and 100
20 Nm³/h of H₂S, is passed through a conventional amine plant, such as, for example, an MDEA plant, thus separating the hydrogen sulphide from the methane.

The hydrogen sulphide, which is desorbed by means of
25 thermal treatment, is joined to an aliquot of the methane

stream in order to have an H_2S concentration equal to 65% moles of the blend, the remaining 35% being methane.

The blend thus obtained, with a total flow-rate of 780 Nm^3/h , after being heated (to $T = 1,050^\circ\text{C}$) in a system of
5 two subsequent heat exchangers, is fed to the reforming reactor, consisting, in this example, of a fixed-bed reactor packed with a catalyst consisting of Cr_2S_3 supported on silica, operating at $T = 950^\circ\text{C}$.

The outgoing fumes consisting of non-reacted CS_2 , hydrogen, H_2S and methane, are sent to a condenser in which
10 CS_2 is separated as a liquid, whereas the stream mainly consisting of hydrogen with small quantities of non-reacted H_2S and methane, is sent back to the amine plant.

The CS_2 which is obtained (149.6 l/h) is fed to the
15 combustion plant together with air, obtaining a stream consisting of CO_2 and SO_2 (at $T = 1,100^\circ\text{C}$). This stream is used for heating the reagents to be fed to the reforming reactor. After transferring its heat to the reagents of the reforming reaction, it can then be fed to a plant for the
20 production of sulphuric acid or disposed of by injecting it into the ground.

CLAIMS

1. A process for the abatement of hydrogen sulphide from compositions containing it with the contemporaneous production of hydrogen, comprising:

- 5 a. feeding a blend comprising methane and hydrogen sulphide to a reforming reactor operating at a temperature ranging from 900 to 1,500°C and at atmospheric pressure or slightly lower, for example between 0.08 and 0.1 MPa, to produce a blend essentially consisting
10 of carbon disulphide (CS₂) and hydrogen (H₂);
- b. cooling the reaction products and separating the carbon disulphide from the remaining reaction blend containing hydrogen;
- c. burning the carbon sulphide with a gas containing oxygen to produce a gaseous blend, essentially consisting
15 of CO₂ and SO₂, at a high temperature;
- d. feeding at least an aliquot of the hot gases of the carbon disulphide combustion to the reforming step, as a heat source for maintaining the endothermic reaction
20 of step (a); and
- e. using the combustion gases of carbon disulphide, coming from step (d), as intermediate products for downstream chemical syntheses or disposing of them by injection into suitable geological structures.
- 25 2. The process according to claim 1, wherein the

blend comprising methane and hydrogen sulphide is a gaseous stream coming from refinery plants or a stream of natural gas coming from production fields, or a gas stream associated with oil fields.

5 3. The process according to claim 1 or 2, wherein the concentration of hydrogen sulphide in the blend ranges from 1 to 65% moles with respect to the total amount.

 4. The process according to any of the previous claims, wherein the reforming reaction is carried out in
10 the presence of a catalyst selected from sulphides of metals of group VIB, VIIB and VIIIB of the periodic system of elements.

 5. The process according to any of the previous claims, wherein the reforming reaction is carried out with
15 $\text{CH}_4/\text{H}_2\text{S}$ molar ratios higher than 0.5.

 6. The process according to any of the previous claims, wherein the products of the reforming reaction are cooled to a temperature lower than 50°C.

 7. The process according to any of the previous
20 claims, wherein the carbon sulphide burned is at least equal to 55% by weight of the total CS_2 produced.

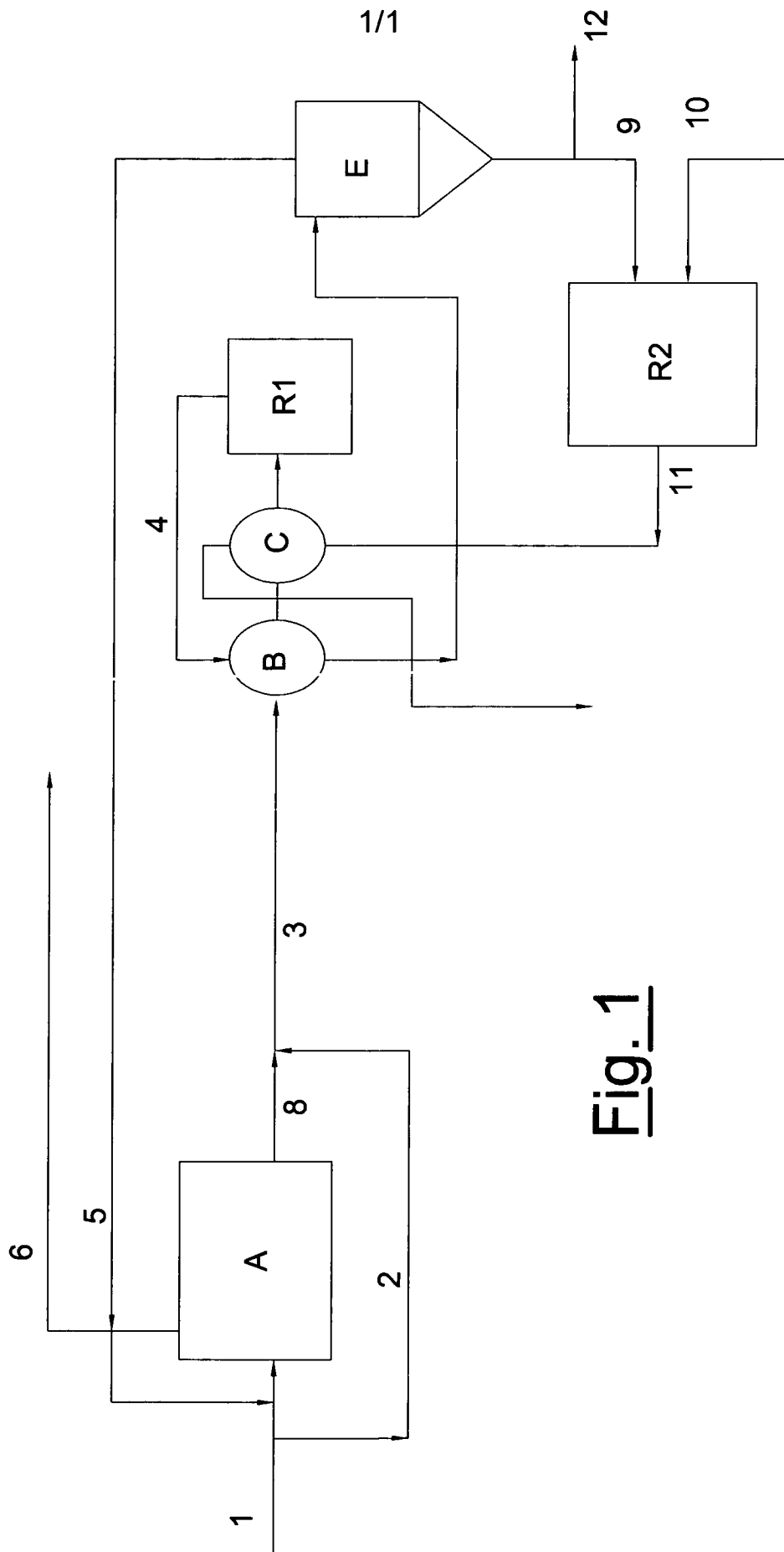


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/001918

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 C01B17/50 C01B31/26

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 788 262 A (ADCOCK WILLIS A ET AL) 9 April 1957 (1957-04-09) column 1, line 30 - column 5, line 7; figure 3	1-7
A	GB 1 126 465 A (IVOR GRAY NIXON) 5 September 1968 (1968-09-05) page 5, line 120 - page 6, line 62; figure 1	1-7
A	GB 293 172 A (IG FARBENINDUSTRIE AG) 5 July 1928 (1928-07-05) page 1, line 15 - page 3, line 55	1-7
A	US 3 388 971 A (SCHUMAN SEYMOUR C) 18 June 1968 (1968-06-18) column 1, line 25 - column 4, line 16; figures 1,2	1-7
	----- -/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2010

Date of mailing of the international search report

14/01/2010

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

Cristescu, Ioana

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/001918

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 10 2004 013283 A1 (GUENNADI BERNER [DE]) 13 October 2005 (2005-10-13) paragraph [0005] - paragraph [0011] -----	1-7
A	US 4 695 443 A (LEON ALBERT M [US]) 22 September 1987 (1987-09-22) column 3, line 26 - column 9, line 20 -----	1-7
A	HUANG ET AL: "Liquid hydrogen production via hydrogen sulfide methane reformation" JOURNAL OF POWER SOURCES, ELSEVIER SA, CH, vol. 175, no. 1, 26 November 2007 (2007-11-26), pages 464-472, XP022361662 ISSN: 0378-7753 paragraph [03.1]; figures 9,10 -----	1-7
A	US 2006/254769 A1 (WANG DEAN C [US] ET AL WANG DEAN CHIEN [US] ET AL) 16 November 2006 (2006-11-16) paragraph [0038] - paragraph [0066] -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/001918

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2788262	A	09-04-1957	NONE	
GB 1126465	A	05-09-1968	NONE	
GB 293172	A	05-07-1928	NONE	
US 3388971	A	18-06-1968	NONE	
DE 102004013283	A1	13-10-2005	NONE	
US 4695443	A	22-09-1987	NONE	
US 2006254769	A1	16-11-2006	AU 2006240103 A1	02-11-2006
			CA 2606215 A1	02-11-2006
			EA 200702287 A1	28-04-2008
			EP 1871988 A2	02-01-2008
			US 2008302532 A1	11-12-2008
			US 2009025935 A1	29-01-2009
			WO 2006115965 A2	02-11-2006