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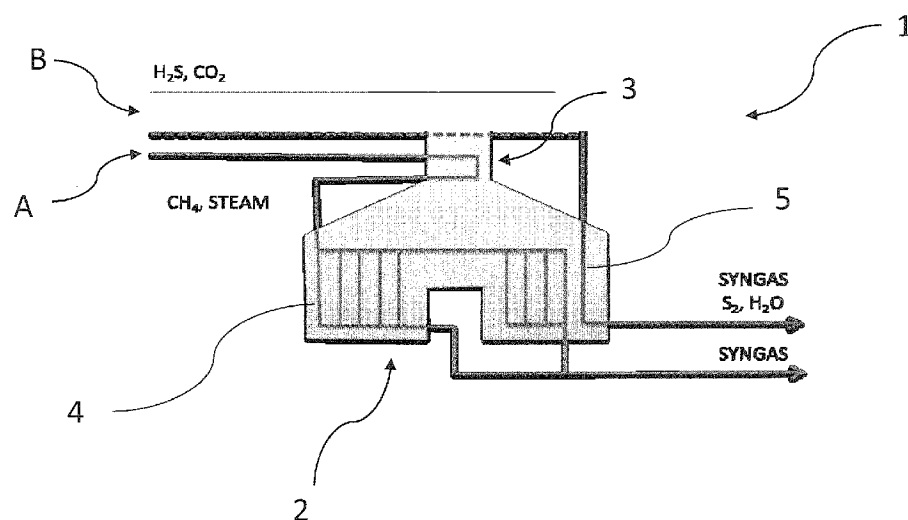


Fig. 1

(57) Abstract: A furnace for gas fields, for refineries, for petrochemical plants, for hydrogen production by gasification and for reforming comprising: - a radiant zone, - a convective zone, - a first and at least a second series of pipes through which at least two segregated process gas flows respectively pass, wherein: • The first process flow enters said furnace at the convective zone and, flowing through said first series of pipes leaves said furnace at the radiant zone, or alternatively, said first process flow enters said furnace at the radiant zone and, flowing through the first series of pipes, leaves the furnace at the radiant zone; • The second process flow, enters said furnace at the convective zone or at the radiant zone and, flowing through said second series of pipes, leaves said furnace at the radiant zone; • Said second series of pipes is made of a material resistant to acid gases.



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FURNACE AND PROCESS FOR SYNTHESIS GAS PRODUCTION

DESCRIPTION

Field of the invention

5 The present invention relates to a furnace for gas fields, for refineries, for petrochemical plants, for hydrogen production by gasification and reforming.

Background

As known any use of fossil fuel source (crude, natural gas, shale gas and oil, coal)
10 and non-fossil fuel source (biomass, biogas, geothermal) leads to the joint production of CO₂ and H₂S in different proportions.

Gases containing such substances in discrete amounts are defined acid gases or tail gases and are being the object of a relevant scientific discussion due to their dramatic impact in terms of global warming and climate change, which they are the main responsible
15 for.

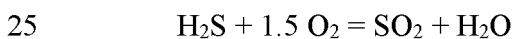
To date acid gases are not being reused, if not only in very small amounts, and the only alternative to releasing them into the atmosphere is to seize and store them in deep waters or remote underground sites. Such extreme measures are in any case being debated as for the possible implementation and efficiency thereof.

20 In WO2015015457A1 to the Applicant it is disclosed using the aforesaid acid gases for producing synthesis gases (CO and H₂ or syngas).

The syngas production takes place according to the following endothermic reaction:



The necessary energy supply is provided by the exothermic reaction:



This process, which in any case is obviously versatile as it can be associated to other productions with few modifications to already existing plants, however requires a considerable amount of activation energy. In fact, the rather high operating temperatures are higher than 800°C and in some cases they overcome 1300°C. Furthermore, oxygen to
5 be used in the second exothermic reaction must be carefully dosed to avoid excessive SO₂ oxidation, which represents a harmful emission, that must be removed for example by means of Claus plants or sulphuric acid production plants.

It is thus perceived the need to find alternative solutions in order to reduce the emission of such gases and possible polluting emissions.

10 US 5878699 discloses a furnace with 3 segregated flows of which.

The first flow does not enter nor leave at any of the radiant or convective zones but at a zone above the convective zone. The other two flows enter and leave only at the radiant zone and at the convective zone only. This plant is employed upstream of a plant for producing methanol, ammonia, hydrogen or syngas. In case of a plant for producing
15 methanol, hydrogen or syngas one of the two convective/radiant zones heats a mixture of hydrocarbons and water, while the second zone heats steam to be used as utility; in the case of ammonia the first cell will serve for heating a mixture of hydrocarbons and steam and the second one for heating a mixture of steam and air.

Summary of the invention

20 In order to overcome the aforesaid problems of WO2015015457A1 a furnace has been conceived wherein, in addition to industrial processes for obtaining intermediate products intended for the synthesis of high added value products, disposal reactions of such harmful emissions can be carried out in particular of acid gases such as CO₂ and H₂S.

25 The object of the present invention is a furnace comprising:

- a radiant zone,

- a convective zone,

said furnace comprising a first and at least a second series of pipes through which at least two segregated process gas flows pass,

5 wherein:

- the first process flow enters said furnace at the convective zone and, flowing through said first series of pipes, leaves said furnace at the radiant zone, or alternatively, said first process flow enters said furnace at the radiant zone and, flowing through the first series of pipes, leaves the furnace at the radiant zone;
- 10 • the second process flow, enters said furnace at the convective zone or at the radiant zone and, flowing through said second series of pipes, leaves said furnace at the radiant zone,
- Said second series of pipes is made of a material resistant to acid gases.

This furnace can be inserted inside refineries, gas fields, reforming plants,
15 petrochemical plants, plants for producing hydrogen by gasification.

LIST OF FIGURES

Figure 1: a schematic representation of a furnace according to an embodiment of the present invention;

20 Figure 2: a schematic representation of a furnace according to an embodiment of the present invention;

Figure 3: a representation in form of block diagram of a steam reforming conventional process;

25 Figure 4: a representation in form of block diagram wherein the furnace according to the embodiments of figure 1 and figure 2 is inserted in a steam reforming process;

Figure 5: a schematic representation of a furnace according to an embodiment of the present invention;

Figure 6: a schematic representation of a furnace according to an embodiment of the present invention;

5 Figure 7: a representation in form of block diagram wherein the furnace according to the embodiments of figure 5 and figure 6 is inserted in a steam reforming process,

Figure 8: a representation in form of block diagram of the flows entering and leaving a conventional furnace used in the steam reforming conventional process of figure 3,

10 Figure 9: a representation in form of block diagram of the comparison between the conventional furnace used in the conventional steam reforming process of figure 3 with the process according to the present invention of figure 4;

Figure 10: a representation in form of block diagram of the comparison between the conventional furnace used in the conventional steam reforming process of figure 3 with
15 the process according to the present invention of figure 7;

DETAILED DESCRIPTION

The conventional-type furnace is mainly dedicated to syngas production by the steam reforming process, which takes place according to the following reaction scheme:

20 R1: $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$.

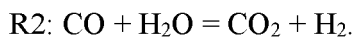
In the block diagram of Figure 3 various steps of this process and the related operative units are reported. In particular, the conventional furnace or steam methane reformer, where the reaction R1 is carried out is indicated by the acronym SMR (Steam Methane Reformer).

25 In this figure 3, upstream of the furnace SMR, raw natural gas is conveyed in a

sweetening unit, hereinafter indicated as SWEETENING unit, thereby acid gases H₂S and CO₂ are separated. Preferably, amine sweetening techniques are used with mixtures of amine/water wherein amines are preferably MEA (methylamine), DEA (diethylamine), MDEA (methyl diethanolamine) or other similarly efficient technologies of (for example Sorption Enhanced, Water-Gas Shift or other hot-separations).

The gas thus purified is conveyed to the SMR unit where the reaction R1 takes place.

In this furnace, steam, preferably exceeding with respect to the stoichiometric ratio, is sent to allow the reaction R1. Gases leaving the SMR, comprising CO, H₂, H₂O and unreacted CH₄ are sent to a Water-Gas Shift Reactor or unit, hereinafter WGSR, where the shift reaction R2 is carried out:



Usually, such reaction R2 is employed in order to adjust the molar ratio between H₂/CO, to optimize morphology and efficiency of the following chemical synthesis (for example, base organic industry or fertilizers) or to maximize the production of hydrogen (for example, refineries or gasification). As known, the reaction direction depends on the operative temperature of the WGSR.

When leaving the WGSR, the process flow is treated in a unit for removing steam or dehydration unit, hereinafter De-W (De-Watering). In particular, such unit for removing steam consists of an apparatus wherein the water contained inside the process flow treated therein is removed, by condensation.

Subsequently, the process flow leaving De-W is sent to a Pressure Swing Adsorption unit, hereinafter PSA. In particular, PSA refers to a unit able to separate at least H₂ and CO₂ in order to maximize H₂ production to be used in following steps. The separated hydrogen is for example sent to a Hydro-DeSulfuration unit, hereafter HDS for example a

catalyst train of the Claus type, for removing sulphur from oil loads before processing thereof.

The conventional furnace, where the reaction R1 takes place, comprises an upper convective zone where the thermal exchange takes place by convection. The lower part, defined as radiant zone, comprises a firebox with one or more vertical and/or horizontal burners, configured to irradiate the series of pipes containing a catalyst typically used to carry out the reaction R1. The convective zone, through which the process fluid entering the conventional furnace passes, is heated by convection by off-gases produced in the radiant zone by combustion of combustible gases in presence of oxygen. Thereby, the entering gas process flow undergoes a pre-heating step.

The furnace that is the object of the present invention is schematically represented in figures 1, 2, 5 and 6 according to acid gases entering the furnace.

As reported above, the furnace 1 is different in that it comprises a first and a second series of pipes. In the first series, indicated by 4, the reaction R1 is carried out, while in the second series, indicated by 5, acid gases which can be a mixture of CO₂ and H₂S or only of H₂S are conveyed.

The series of pipes (5), being intended for acid gases, consists of material resistant to acid gases.

It is also well known to the expert in the art, what kind of material can be used, as a material resistant to acid gases must stand high temperatures, highly corrosive acid gas flows.

According to a preferred solution said series of pipes 5 can be partially shielded by self-propelled walls limiting heating with respect to the pipes of series 4.

The furnace 1 can be designed with three distinct variants.

First Variant (figure 1 and figure 5)

In the first variant the first process flow A. entering the furnace 1, comprising a mixture of natural gas, preferably methane and steam, is treated in the same way as in an above-described conventional SMR-type furnace. In other words, methane and steam, the latter preferably exceeding with respect to the stoichiometric ratio, firstly pass through the convective zone 3, then through the radiant zone 2. While passing through the radiant zone 2 the first process flow is subdivided in the first series of pipes 4 where the reaction R1 takes place. The first process flow leaving the furnace 1 from the side of the radiant zone 2 comprises a mixture of CO and H₂ and optionally unreacted methane and steam. The reaction R1 is carried out at a temperature between 550°C and 1050°C, preferably between 750°C and 900°C, more preferably the reaction R1 is carried out at a temperature of 800°C. For the purposes of the present invention the pressure of the first process flow inside the furnace is at least comprised between 1 bar and 50 bars, preferably between 10 bars and 40 bars and more preferably the pressure of the first process flow is of 20 bars.

The second process flow consists of a mixture of acid gases comprising a combination of H₂S and CO₂ in figure 1 and only H₂S in figure 5. Thereby acid gases can be treated increasing the production of hydrogen for following treatments such as for example HDS and for reducing inlets of CO₂ and of other waste products.

The second process flow entering the furnace 1 according to the first variant passes through the convective zone 3 and then to the radiant zone 2 as shown in figures 1 and 5. The second series of pipes 5 is not provided with a catalyst.

Second Variant (figure 2 and figure 6)

In the second variant the first process flow A. entering the furnace 1, comprising a mixture of natural gas, preferably methane and steam, is treated in the same way as in an

above-described conventional SMR-type furnace.

In the second variant the second process flow B., entering the furnace comprising a mixture of CO₂ and H₂S (figure 2) or only H₂S (figure 6) via an outer bypass is directly sent to the radiant zone 2 passing through the second series of pipes 5.

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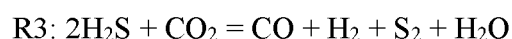
Third Variant (Not shown)

In the third variant the first process flow of process A. entering the furnace 1 comprising a mixture of natural gas, preferably methane, and steam is sent directly to the radiant zone 2 and passing through the series of pipes 4 it leaves the radiant zone.

10 Furthermore, the second process flow B., entering the furnace comprising a mixture of CO₂ and H₂S or only H₂S via an outer bypass is directly sent to the radiant zone 2 passing through the second series of pipes 5.

The choice among the variants may be determined by the conditions envisaged during the step of designing the construction of a new plant or in redesigning the furnace 1 in revamping cases when a conventional SMR furnace is to be converted into a furnace according to the present invention.

In figures 4 a preferred embodiment of a plant wherein the furnace 1 is inserted is described. In this case, the second entering process flow comprises a mixture of H₂S and CO₂. Such mixture is sent to the second series of pipes 5 of the furnace 1 where the endothermic reaction R3 takes place:



For the purposes of the present invention the part of the furnace where the reaction R1 takes place is identified as SMR, while the part of the furnace wherein the reaction R3

25

takes place is called Enhanced Steam Methane Reformer hereinafter ESMR as indicated in the present figure 4 and in the following ones.

Thus, the furnace 1, according to the present invention, comprises both an SMR part and an ESMR part.

5 Preferably, the reaction R3 is carried out at least in a range of temperatures between 550°C and 1050°C, preferably between 700°C and 900°C, more preferably the reaction R3 is carried out at a temperatures of 850°C.

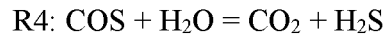
It must be noted that the pressure of the second process flow inside the furnace is at least comprised in a range between 0.01 bar and 50 bars, preferably between 0.5 bar and 10 25 bars, more preferably the pressure of the second process flow inside the furnace is between 1 bar and 5 bars.

According to the present invention the residence times of the second process flow inside the ESMR are comprised between 0.1 and 5 seconds, preferably between 0.5 and 2 seconds.

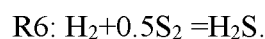
15 In the ESMR the conversion of the entering acid gases such as CO₂ and H₂S takes place. The second process flow leaving the second series of pipes 5 comprises a mixture of CO, H₂, S₂, H₂O, unreacted acid gases, COS and CS₂, which is sent to a unit for removing water and sulphur hereinafter identified by the acronym De-W and De-S in which H₂O and S₂ partially separate by condensation from the leaving mixture . In particular, for the 20 purposes of the present invention, unit for removing sulphur or De-Sulfuration unit, De-S, refers to a conventional-type of separator configured to remove sulphur contained inside the treated process flow.

Preferably, the process flow leaving De-W and De-S comprising residual H₂O, S₂ as steam, COS, CS₂, CO, H₂ and unreacted acid gases is treated in order to remove 25 impurities and obtain H₂ as pure as possible. For these reasons the process flow is treated

through hydrolysis and hydrogenation reactions of sulphur vapours. In particular, the process flow leaving De-W and De-S is submitted to a gamma-alumina-catalysed reactor wherein the following reactions, R4, R5 are carried out:



as well as the hydrogenation reaction of sulphur vapours R6



In reactions R4 and R5 water is present in minimum quantities (as well as COS and CS₂) as the majority of water was removed in the De-W unit.

10 Advantageously, the selectivity of the whole process is equal to 100% in syngas (CO and H₂), elemental sulphur and water.

Subsequently, the process flow leaving the catalysed reactor comprising H₂S, CO₂, CO, H₂ is sent to a SWEETENING unit where H₂S and CO₂ are separated from CO and H₂.

15 In particular, the mixture of H₂S and CO₂ is recycled at the entrance of the furnace 1 and conveyed in the second process flow entering the ESMR where the reaction R3 takes place. Vice versa, the mixture containing CO and H₂ is sent to the WGSR to increase the production of H₂.

Advantageously, a pre-existing WGSR does not need structural modifications as in
20 this case the amount of syngas, CO and H₂, obtained by converting acid gases in the WGSR is preferably equal to the no longer necessary quantity coming from the reforming of SMR methane.

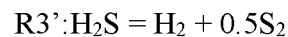
Advantageously, the use of the furnace according to the present invention formed by SMR + ESMR allows to activate a hydrogen recirculation inside the plant. Such
25 recirculation reduces in turn the methane load at the entrance of the SMR unit of the furnace

1 with a series of advantageously secondary effects:

- Reduction of the steam to be supplied to the unit;
- Reduction of the amount of methane to be supplied to firebox;
- Reduction of the stoichiometric combustion air at the firebox.

5 In addition to the already mentioned reduction of entering methane, such effects contribute to reduce the off-gas flow rate leaving the head of the furnace 1 and the CO₂ flow rate released by the PSA unit. The reduction of further emissions adds to these advantages due to the lack of combustion of acid gases in the traditional Sulphur Recovery Units (SRUs), such as for example, the Claus trains.

10 In figure 7 a preferred embodiment of a plant wherein the furnace 1 is inserted is disclosed. In particular, the second entering process flow comprises a mixture of H₂S. In detail, the second entering process flow is conveyed in the second series of pipes 5 where the pyrolysis reaction R3' is carried out:



15

For the purposes of the present invention the part of the furnace wherein the reaction R1 takes place is identified as SMR, while the part of the furnace wherein the reaction R3' takes place is called Sulphidric Acid Thermal Splitting, hereinafter SATS as indicated in the figures.

20 Therefore, the furnace 1, according to an embodiment comprises a SMR reaction and a section where the aforesaid reaction takes place identified hereinafter with the acronym SATS.

The R3' reaction is carried out at least in a range of temperatures between 550°C and 1050°C, preferably between 700°C and 900°C, more preferably the R3' reaction is
25 carried out at a temperature of 850°C.

Preferably, it is possible to take advantage of the conventional SMR burners to carry out the reaction R3' at temperatures higher than the R1 ones.

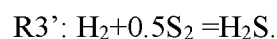
The pressure of the second process flow inside the furnace is at least comprised in a range between 0.01 bar and 50 bars, preferably between 0.5 bar and 25 bar, more preferably the pressure of the second process flow inside the furnace is between 1 bar and 5 bars.

According to the present invention the residence times of the second process flow inside the SATS are comprised between 0.1 and 5 seconds, preferably between 0.5 and 2 seconds.

In this case, the second process flow leaving said second series of pipes, SATS, comprising a mixture of unreacted H₂, S₂, H₂S, is sent to De-S where it partially separates by condensation S₂ from the mixture.

Advantageously, since other reaction products and/or by-products are absent, the selectivity of the whole process is equal to 100% of hydrogen and yield is similarly complete thanks to the recycles described hereinafter.

Preferably, the process flow leaving De-S comprising unreacted S₂, H₂ and H₂S, is submitted in a reactor to the reaction R6 of hydrogenation of sulphur vapours:



Separating the hydrogen produced from the remaining unreacted H₂S can be implemented according to different implementation modes, i.e. by a SWEETENING-3 unit, as described above. In particular, the process flow leaving the reactor comprising H₂S and H₂ is sent to the SWEETENING-3 unit wherein H₂S is separated from H₂.

Subsequently, H₂S is recycled and conveyed into the second process flow entering said furnace where the R3' reaction takes place.

By contrast hydrogen leaving the SWEETENING-3 unit is sent to the PSA unit. Alternatively, H₂ coming from the SWEETENING unit is conveyed with the process flow leaving De-W upstream of the PSA unit where hydrogen H₂ is separated from CO₂.

Advantageously, SMR+SATS allows to activate a hydrogen recirculation inside the plant. Such recirculation reduces in turn the methane load at the entrance of the SATS unit resulting in a series of advantageously secondary effects:

- Reduction of the steam to be supplied to the unit;
- Reduction of the amount of methane to be supplied to firebox;
- Reduction of the stoichiometric combustion air at the firebox.

In addition to the already mentioned reduction of entering methane, such effects contribute to reduce the off-gas flow rate leaving the head of the furnace 1 and the CO₂ flow rate released by the PSA unit. The reduction of further emissions adds to these advantages due to the lack of H₂S combustion in the traditional Sulphur Recovery Units (SRUs), such as, for example, the Claus trains.

It must be noted that in both cases of figures 4 and 7 the first and the second process flow entering said furnace come from at least a sweetening unit which receives raw natural gas, comprising a mixture of methane, CO₂ and H₂S.

Specifically, the gas mixture of the first process flow containing methane with added steam, for carrying out the reforming reaction, is treated with a SWEETENING unit configured to separate H₂S, CO₂ from methane.

Preferably in the case of figure 4, the raw natural gas is treated by a first SWEETENING unit configured to separate methane from the mixture of H₂S and CO₂. Thereby methane is sent to the SMR unit as first process flow and the mixture comprising H₂S and CO₂ is sent to the ESMR unit as second process flow.

Preferably in the case of Figure 7, the raw natural gas is treated by a first

SWEETENING -1 unit configured to separate H₂S from the mixture containing natural gas and CO₂. Thereby, H₂S is sent as a second process flow to the SATS unit, while the mixture containing natural gas and CO₂ is sent to a second SWEETENING-2 unit configured to separate CO₂ from natural gas. Thereby, the separated natural gas is sent to the SMR unit as first process flow while the separated CO₂ is recycled or treated.

EXAMPLE 1: COMPARISON BETWEEN CONVENTIONAL SMR PROCESS (figure 3) AND SMR-ESMR PROCESS ACCORDING TO THE PRESENT INVENTION (figure 4)

The simulation of the SMR+ESMR apparatus was carried out by means of DSmoke, a computing software for analysing and verifying conversion thermal systems (pyrolysis and combustion) developed at the Centre for Sustainable Process Engineering (SuPER) of the Polytechnic University of Milan. Dsmoke is a software based on a kinetic (30k reactions) and thermodynamic (NIST) database validated by experimental data and industrially present in more than 40 applications. Dsmoke results were integrated in the simulation suite PRO/II (by Schneider-Electric).

SMR base case

The selected base case for assessing and comparing performances of a SMR with the new ESMR or SATS apparatus (dealt with in the following example) is reported in Table 1. For the base case, the process diagram of Figure 3 is taken into consideration, an SMR conventional furnace wherein the second series of pipes is absent thus without ESMR, and the relevant results obtained with the Commercial Suite PRO/II® (by Schneider-Electric) are summarized in Figure 8. In particular, it can be noted that hydrogen production by SMR is equal to 228.4 kg/h.

25

Table 1. Flow rate and composition coming from a gas field (Caspian Sea).

	<i>Molar Composition</i>	<i>Molar flow [kmol/h]</i>	<i>Mass Flow [kg/h]</i>	<i>Mass Flow [ton/day]</i>
N2	2.00%	31.250	875.000	21.000
CO2	15.00%	234.375	10312.500	247.500
H2S	25.00%	390.625	13281.250	318.750
CH4	50.00%	781.250	12500.000	300.000
C2H6	2.00%	31.250	937.500	22.500
C3H8	1.00%	15.625	687.500	16.500
C4H10	1.00%	15.625	906.250	21.750
C5H12	1.00%	15.625	1125.000	27.000
C6H14	3.00%	46.875	4031.250	96.750
TOT	100.00%	1562.500	44656.250	1071.750

The process scheme for ESMR+SMR in a gas field according to the present invention is represented in Figure 4. The invention, ESMR combined with the conventional SMR, does not only receive the natural gas (NG) coming from the sweetening, but, unlike the conventional SMR, also receives the stream of acid gases, H₂S and CO₂ in the second series of pipes, non-catalytic and dedicated to R3 reaction. Acid gases converted by the ESMR are sent to known systems for separating sulphur and optional dewatering and, upon separation of unreacted gases and recirculation thereof upstream of the ESMR, the obtained syngas is sent to the WGSR section, together with syngas coming from the pipe zone dedicated to methane/steam SMR.

The syngas obtained, therefore, has a flow rate contribution resulting from the conventional reforming transformation R1 and an additional portion deriving from R3 reaction. The overall syngas flow rate can be used as it is or it can be shifted to hydrogen or syngas of different qualities.

The advantages of the invention obtained with the Commercial Suite PRO/II® (by Schneider-Electric) are summarized in Figure 9. The analysis is carried out with ESMR at 900°C and 1.8 bar for pipes dedicated to acid gas, with a once-through conversion for each single pipe equal to 17% and subsequent recycling of unreacted products. As a whole, it derives that, being conditions and supply equal to the conventional SMR, the invention ESMR+SMR allows to:

1. Increase hydrogen production from 228.4 kg/h to 252 kg/h (+10.33%)
2. Reduce the steam request for the steam reforming unit (-20.67%)
3. Reduce off-gases released in the atmosphere with respect to the SMR (-16.5%)
4. Reduce CO₂ emissions from the PSA unit (-10.33%)

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EXAMPLE 2: COMPARISON BETWEEN CONVENTIONAL SMR PROCESS (figure 3) AND SMR+SATS ACCORDING TO THE PRESENT INVENTION (figure 7)

The process diagram for the SMR+SATS in a gas field is represented in Figure 7. The invention, SMR+SATS, does not only receive the natural gas (NG) coming from the sweetening, but, unlike the conventional SMR, also receives the stream of H₂S in the zone of non-catalytic pipes and devoted to conversion R3'. The effluents leaving the SATS are sent to known systems for separating sulphur and optional dewatering, and, upon separation of unreacted products and recirculation thereof upstream of the SATS, the obtained hydrogen is sent downstream of the WGSR section, entering PSA or directly to the HDS, together with hydrogen obtained from the SMR portion dedicated to the methane/vapour reforming.

The syngas obtained, therefore, has a flow rate contribution resulting from the conventional reforming transformation R1 and an additional portion deriving from R3' reaction. The overall syngas flow rate can be used as it is or it can be shifted to hydrogen or syngas of different qualities.

The advantages of the invention obtained with the Commercial Suite PRO/II® (by Schneider-Electric) are summarized in Figure 10. The analysis is carried out with SMR+SATS at 900°C and 1.8 bar for pipes dedicated to acid gas, with a once-through conversion for each single pipe equal to 17% and subsequent recycling of unreacted products. As a whole, it derives that, being conditions and supply equal to the conventional

SMR, the invention SMR+SATS allows to:

1. Increase hydrogen production from 228.4 kg/h to 261.05 kg/h (+14.3%)
2. Reduce the steam request for the steam reforming unit (-28.6%)
3. Reduce off-gases released in the atmosphere with respect to the SMR (-23.6%)
- 5 4. Reduce CO₂ emissions from the PSA unit (-14.3%)

CLAIMS

1. A furnace (1) for gas fields, for refineries, for petrochemical plants and for the reforming

5 process comprising:

- a radiant zone (2),

- a convective zone (3)

- a first (4) and at least a second (5) series of pipes through which at least two segregated process gas flows (A) and (B) respectively pass,

10 wherein:

- said first process flow (A) enters said furnace (1) at the convective zone (3) and flowing through said first series of pipes (4) leaves said furnace at the radiant zone (2), or alternatively, said first process flow (A) enters said furnace (1) at the radiant zone (2) and, flowing through the first series of pipes (4), leaves the furnace at the radiant

15 zone (2);

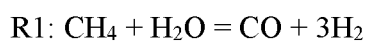
- said second process flow (B), enters said furnace (1) at the convective zone (3) or at the radiant zone (2) and, flowing through said second series of pipes (5), leaves said furnace (1) at the radiant zone (2)

- said second series of pipes (5) is made of a material resistant to acid gases

20 2. A process for producing syngas, comprising the following phases being carried out in the furnace (1) according to claim 1:

- the first process flow (A) enters the furnace (1) comprising a mixture of methane and steam passes by the first series of pipes (4), wherein at the radiant zone (2) syngas is produced according to the steam reforming reaction R1 (SMR):

25



said first series of pipes (4), at least at the radiant zone 2, comprising a tube bundle containing a conventional catalyst suitable for carrying out the reaction R1.

- acid gases of the second entering process flow comprise a mixture of CO₂ and H₂S;

- the second flow (B), which enters the furnace (1), comprises acid gases CO₂ and H₂S and
5 in the second series of pipes (5), at the radiant zone, the reaction R3 (**ESMR**) is carried out:



3. The process according to claim 2, wherein the reaction R3 takes place at least in a
10 temperature range between 550°C and 1050°C, preferably between 700°C and 900°C, more preferably the reaction R3 takes place at a temperature of 850°C.

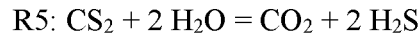
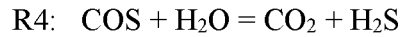
4. The process according to claim 2 or 3, wherein the pressure of the second process flow inside the furnace is at least in a range between 0.01 bar and 50 bar, preferably between 0.5
15 bar and 25 bar, more preferably between 1 and 5 bar.

5. The process according to any one of claims 2 to 4, further comprising the following steps:

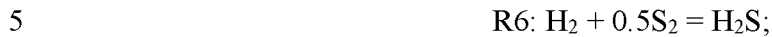
- the second process flow (B)/(**ESMR**) leaving said second series of pipes (5) of the furnace
20 (1) and comprising a mixture of CO, H₂, S₂, H₂O, unreacted acid gases, COS and CS₂ is sent to a dehydration and desulfurization unit (**De-W, De-S**) where H₂O and S₂ are partially separated from the mixture by condensation,

- the process flow leaving the dehydration and desulfurization unit (**De-W, De-S**) comprising H₂O, S, COS, CS₂, CO, H₂ and unreacted acid gases is placed in a gamma-
25 alumina based catalysed reactor (**CONVERTER**) where the following reactions take

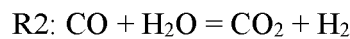
place:



as well as the hydrogenation reaction of sulphur vapours



- the mixture of H_2 and CO coming from the sweetening reaction (**SWEETENING**) is conveyed to a water gas shift reactor (**WGSR**) where the reaction R2 takes place



10 - the first process flow (A)/(**SMR**) leaving the furnace (1) is sent to the same water gas shift reactor (**WGSR**) where the shift reaction R2 takes place;

- the process flow leaving the water gas shift reactor (**WGSR**) is sent to a dehydration unit (**De-W**);

- the process flow leaving the dehydration unit is sent to a pressure swing adsorption unit (**PSA**) where CO_2 and H_2 are separated.

15 - the process flow leaving the catalysed reactor comprising H_2S , CO_2 , CO , H_2 is sent to a sweetening unit (**SWEETENING**) where H_2S and CO_2 are separated from CO and H_2 ,

- the mixture comprising H_2S and CO_2 is recycled and conveyed to the second process flow entering the furnace where the R3 reaction (**ESMR**) takes place,

20 **6.** A process for producing syngas, comprising the following phases being carried out in the furnace according to claim 1:

- the first process flow (A)) comprising a mixture of methane and steam enters the furnace (1) passes through the first series of pipes (4), wherein at the radiant zone (2) syngas is produced according to the steam reforming reaction R1 (**SMR**):



said first series of pipes (4), at least at the radiant zone (2), comprising a tube bundle containing a conventional catalyst suitable for carrying out the reaction R1;

- the second flow (B) comprising the acid gas H₂S enters the furnace (1) passes through the second series of pipes (5) wherein at the radiant zone (2) the reaction R3' (SATS) takes

5 place:



7. The process according to claim 6, wherein the reaction R3' takes place at least in a temperature range between 550°C and 1050°C, preferably between 700°C and 900°C,
10 more preferably the reaction R3' takes place at a temperature of 850°C.

8. The process according to claims 6 or 7, wherein the pressure of the second process flow inside the furnace is at least in a range between 0.01 bar and 50 bar, preferably between 0.5 bar and 25 bar, more preferably between 1 and 5 bar.

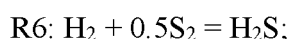
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9. The process according to any one of claims 6 to 8, further comprising the following steps:

- the second process flow (B)/(SATS) leaving said second series of pipes (5) of the furnace (1) comprising a mixture of unreacted H₂, S₂, H₂S is sent to a de-sulfurization unit (De-S)

20 wherein it partially separates by condensation S₂ from the mixture,

- the process flow leaving the desulphurization unit comprising S₂, H₂ and unreacted H₂S is subjected in a reactor (CONVERTER) to the sulphur vapour hydrogenation reaction according to the reaction scheme:

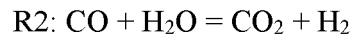


25 - the process flow leaving the reactor comprising H₂S and H₂ is sent to a sweetening unit

(**SWEETENING-3**), where H₂S is separated from H₂,

- the separated H₂S is recycled and conveyed to the second process flow entering the furnace where the R3' reaction (**SATS**) takes place,

-the first process flow (A)/(**SMR**) leaving said furnace (1) is sent to a water gas shift
5 reactor (**WGSR**) where the reaction R2 takes place



and the flow leaving said water gas shift reactor are conveyed to a dewatering unit (**De-
W**),

- the H₂ coming from the sweetening unit (**SWEETENING-3**) is conveyed with the
10 process flow leaving the dehydration unit upstream of a pressure swing adsorption unit
(**PSA**) where the hydrogen H₂ is separated from the CO₂,

10. The process according to any one of claims 5 and 9, wherein the first and the second
process flow entering said furnace (1) come from at least one sweetening unit
15 (**SWEETENING**, **SWEETENING-1**, **SWEETENING-2**) receiving incoming raw
natural gas comprising a mixture of methane, CO₂ and H₂S.

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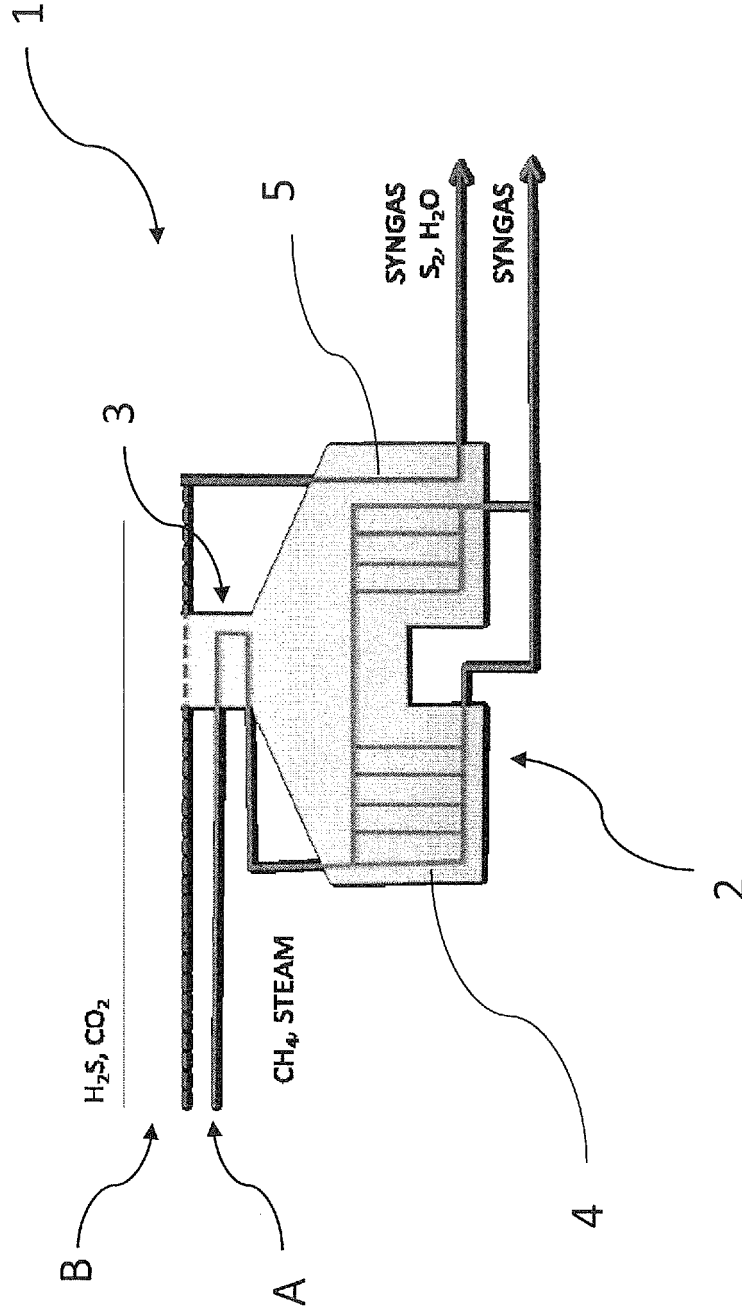


Fig. 1

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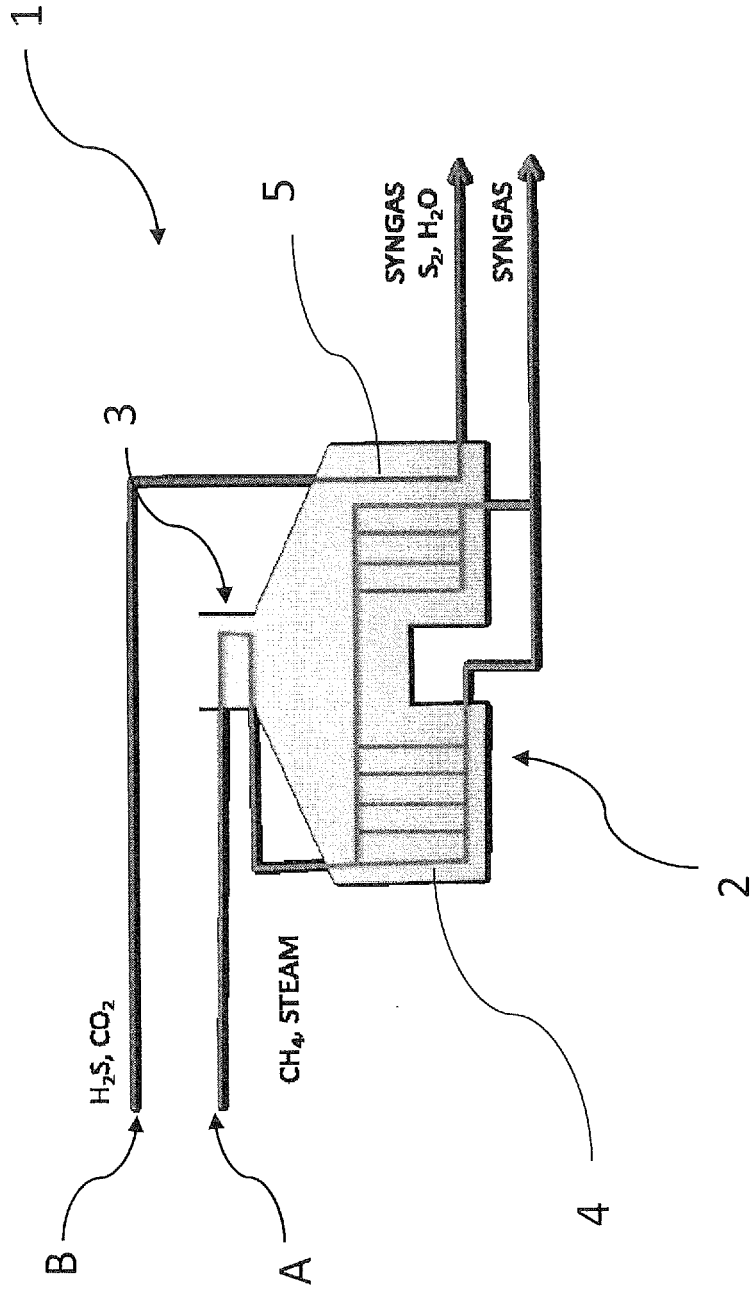


Fig. 2

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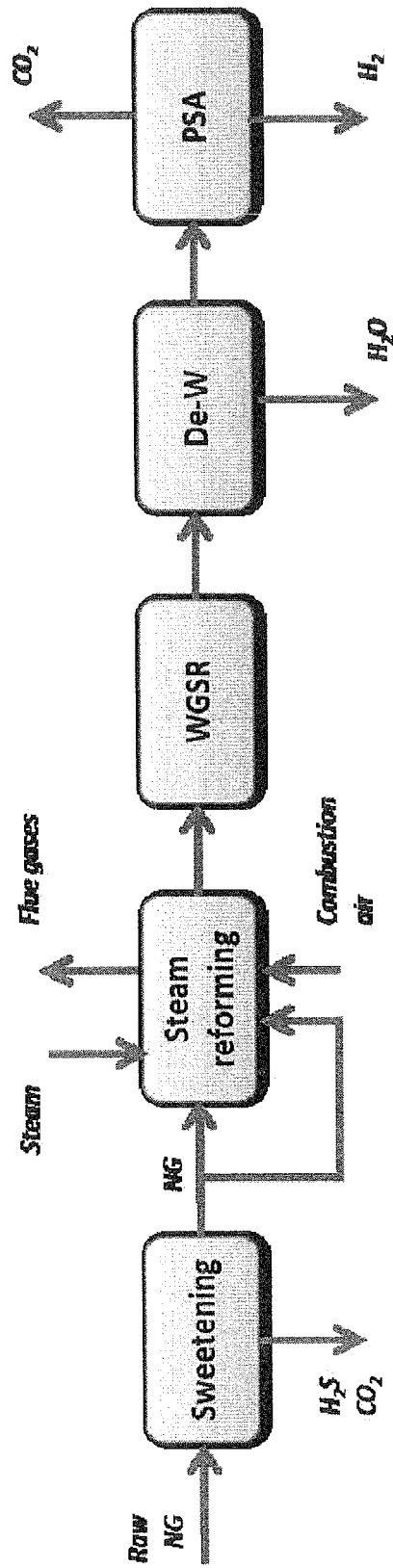


Fig. 3

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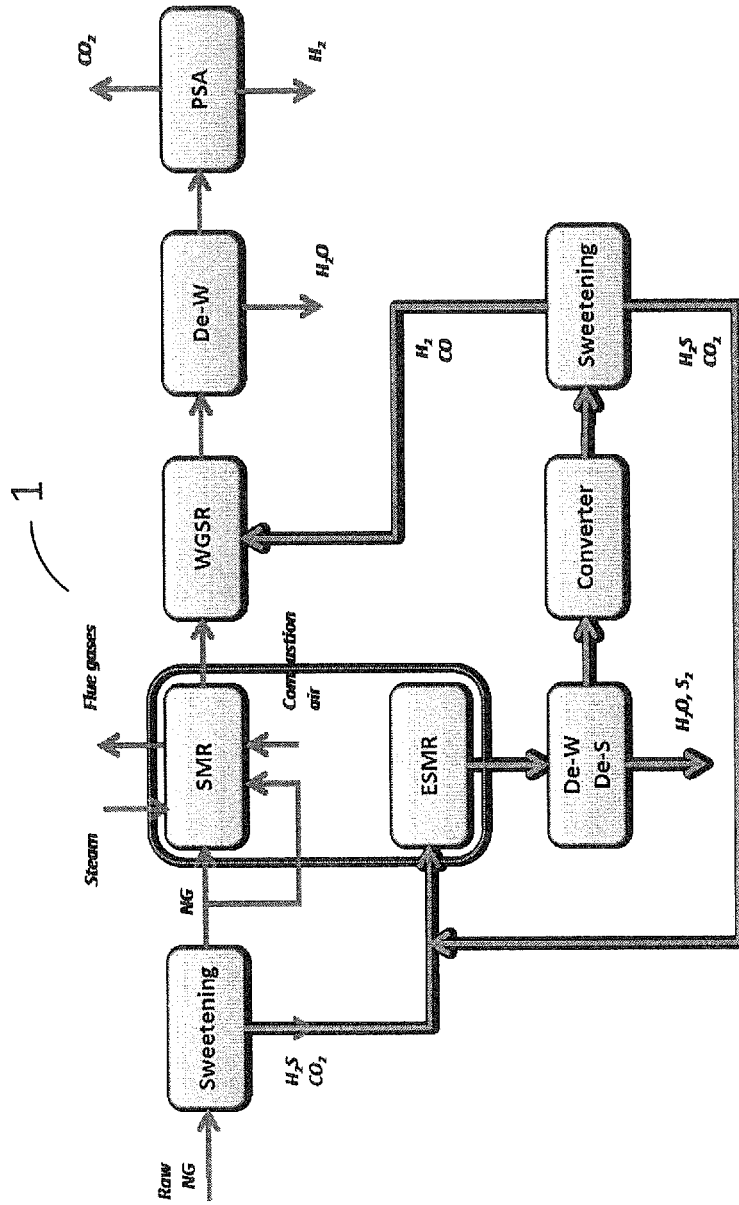


Fig. 4

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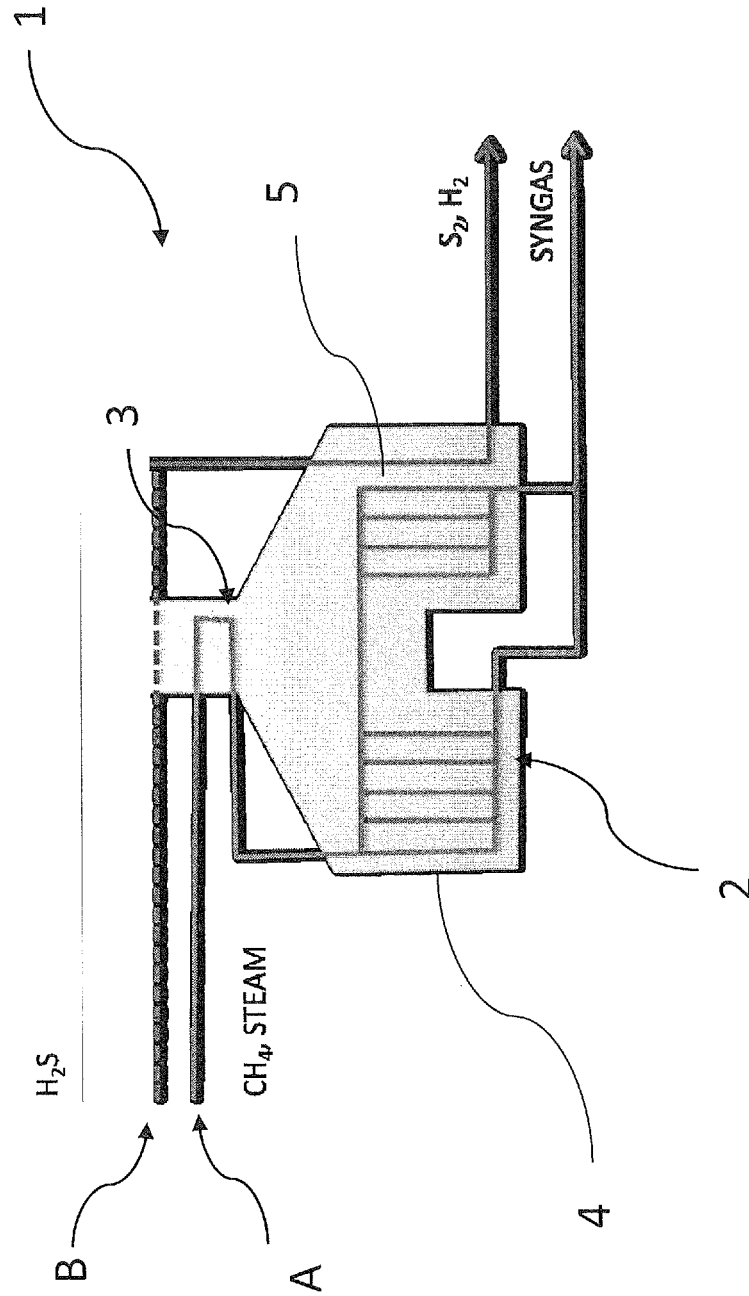


Fig. 5

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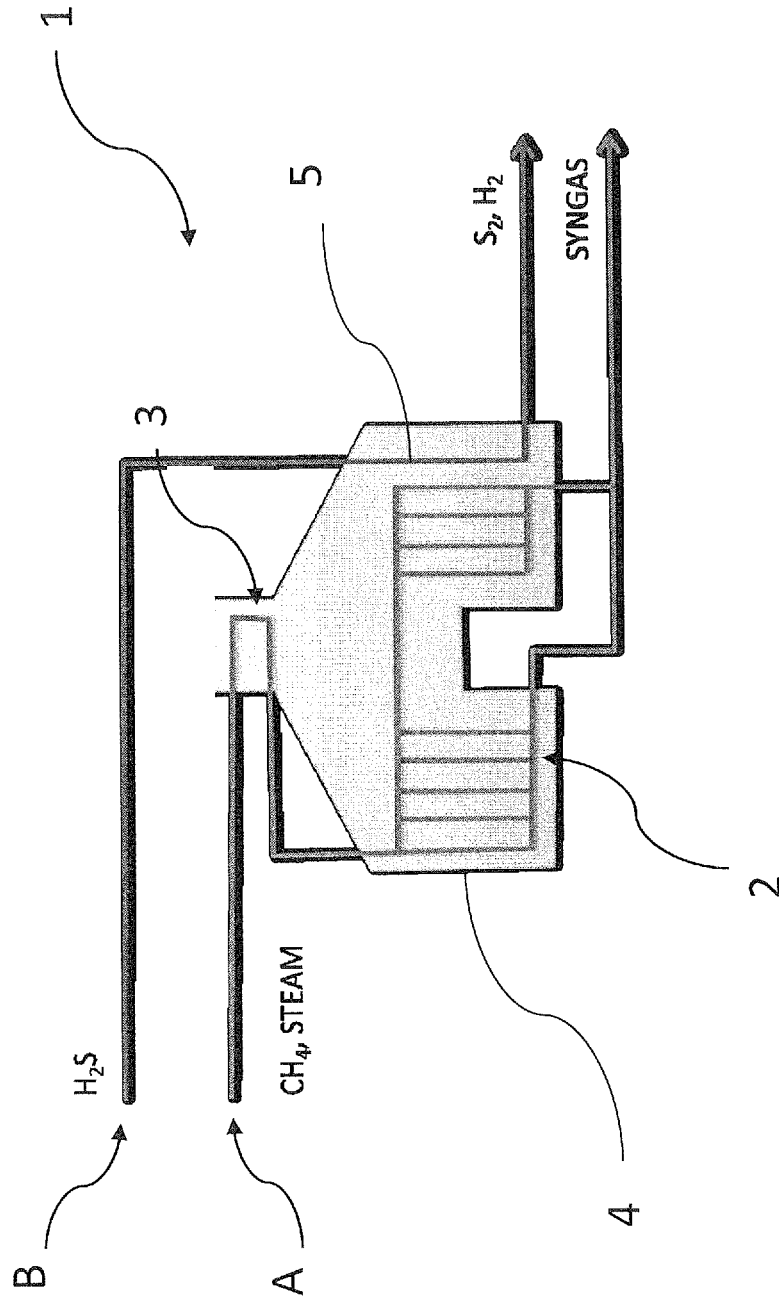


Fig. 6

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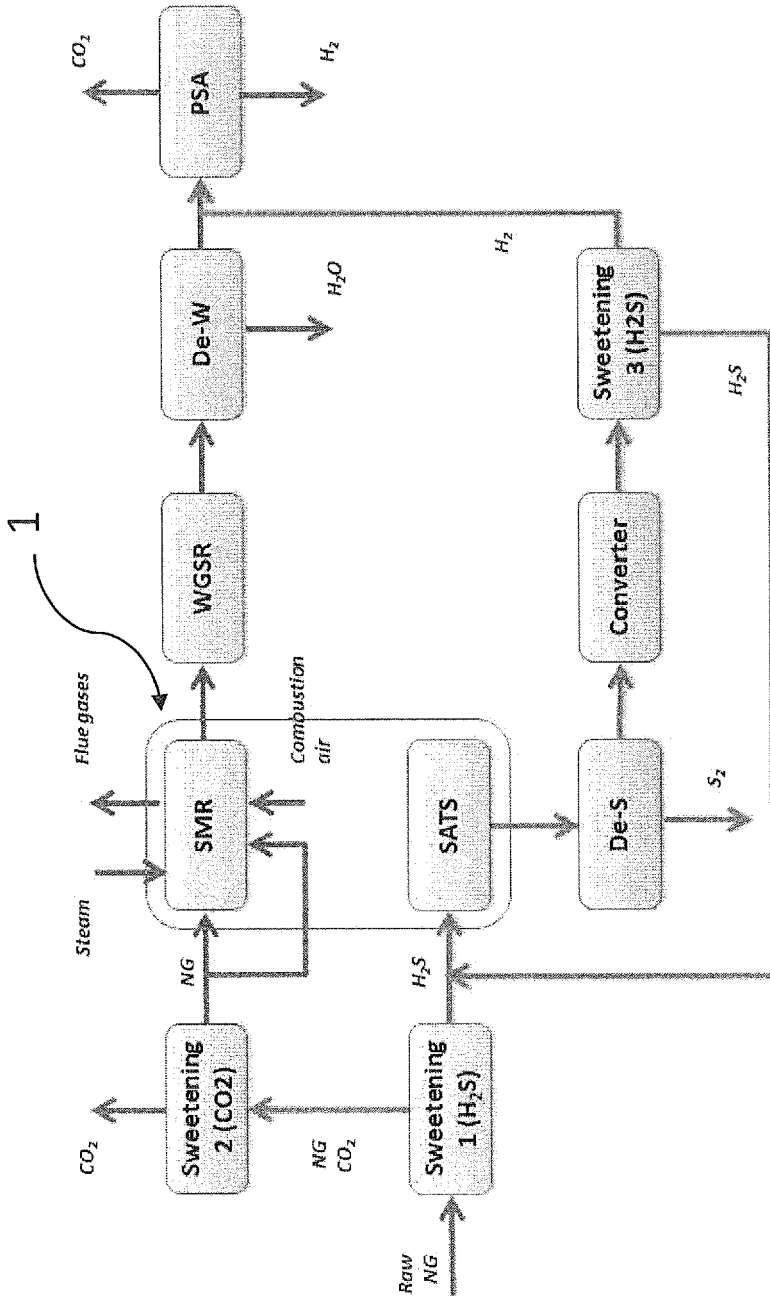


Fig. 7

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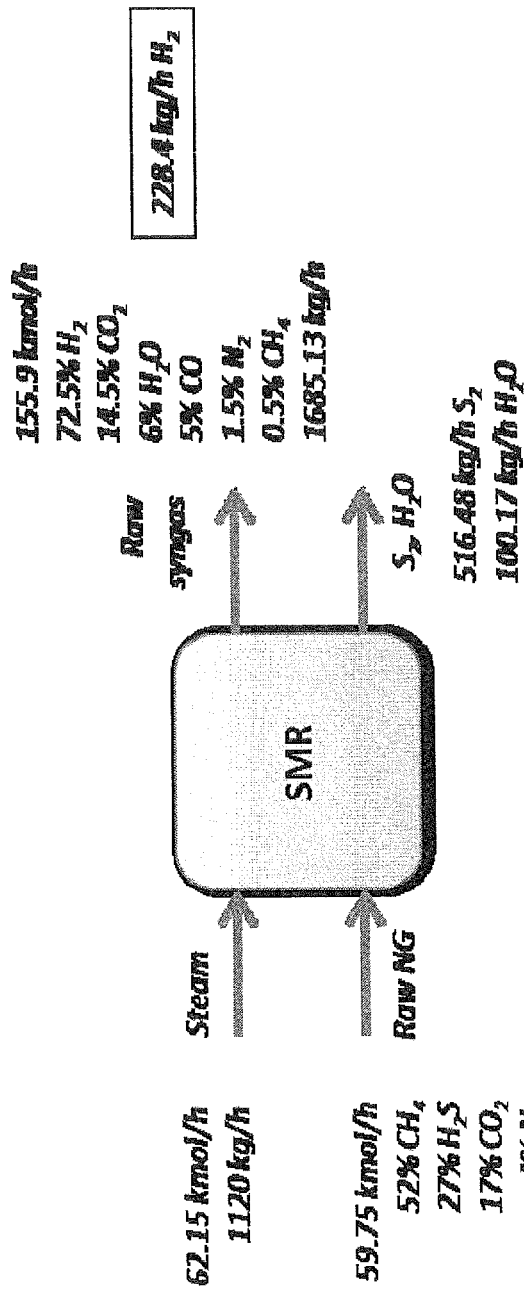


Fig. 8

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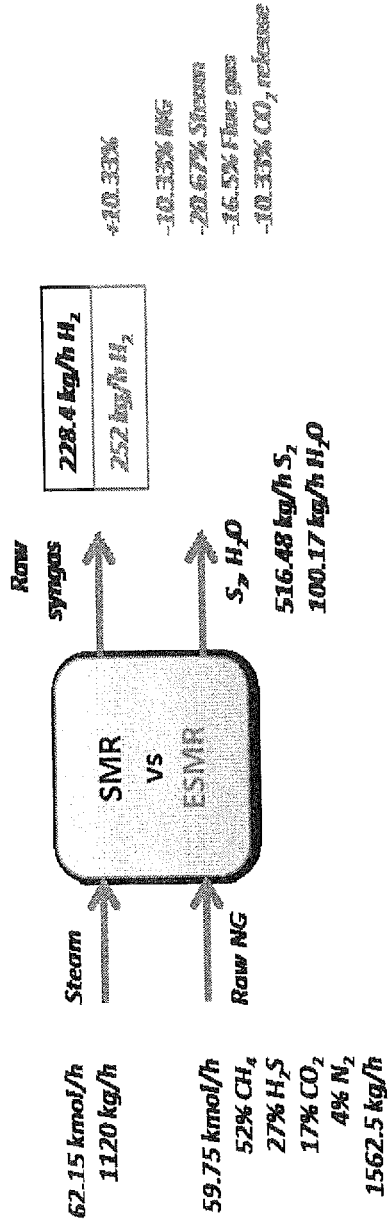


Fig. 9

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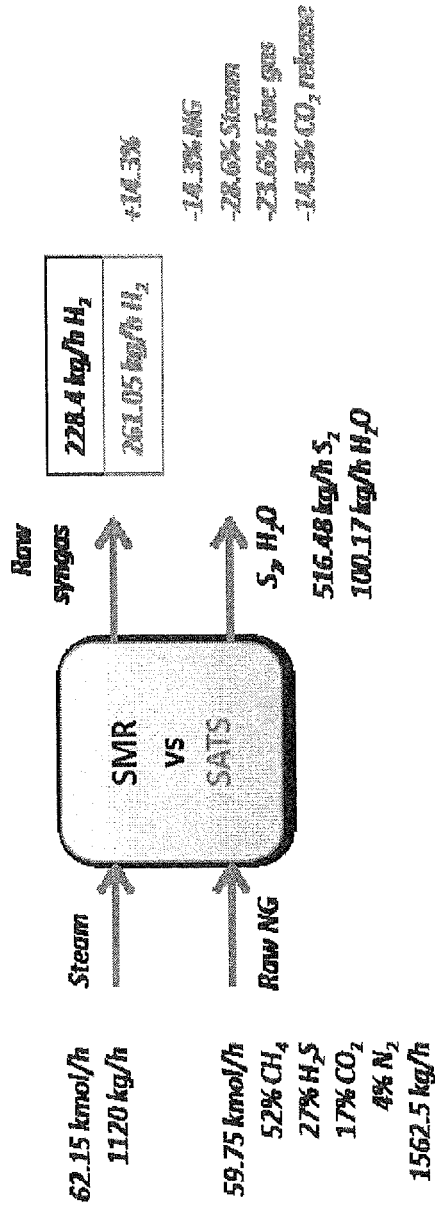


Fig. 10

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/054605

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C01B3/06	B01J8/06	C01B3/38
C01B3/56	C01B17/04	C01B3/48
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 B01J		
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 5 878 699 A (BARNETT DANIEL J [US] ET AL) 9 March 1999 (1999-03-09)	1
A	column 3, line 5 - line 25; figure 1 -----	2-10
A	WO 2015/015457 A1 (MILANO POLITECNICO [IT]) 5 February 2015 (2015-02-05) cited in the application the whole document -----	1-10
	-/--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search	Date of mailing of the international search report	
4 August 2020	14/08/2020	
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 Harf-Bapin, E	

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2020/054605

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>M. GROISIL ET AL: "Numerical Examination of Acid Gas for Syngas and Sulfur Recovery", ENERGY PROCEDIA, vol. 75, no. 75, 1 August 2015 (2015-08-01), pages 3066-3070, XP055719978, NL ISSN: 1876-6102, DOI: 10.1016/j.egypro.2015.07.628 the whole document</p> <p align="center">-----</p>	1-10

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