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(54) **Title:** SYNGAS PRODUCTION BY CO₂ REDUCTION PROCESS

(57) **Abstract:** A process for producing synthesis gas (syngas) comprising the endothermic reaction between CO₂ and H₂S, wherein the energetic supply is provided by the exothermic oxidation of a small portion of H₂S to SO₂ according to the following reaction scheme: R2: H₂S + 1.5 O₂ → SO₂ + H₂O said process being carried out according to the following overall theoretical reaction scheme R1, not taking into account the aforementioned exothermic reaction R2, R1: CO₂ + 2 H₂S → CO + H₂ + S₂ + H₂O wherein the amount of fed oxygen is comprised between 5% and 25% by volume over the total volume of fed reactants gaseous mixture.



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SYNGAS PRODUCTION BY CO₂ REDUCTION PROCESS

FIELD OF THE INVENTION

The present invention relates a production process of synthesis gas starting from CO₂ and H₂S, said reactants being generated by industrial conventional processes or separated by conventional industrial purification processes.

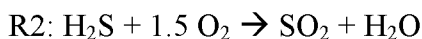
BACKGROUND OF THE INVENTION

Synthesis gas (syngas) is mainly obtained by partial oxidation of hydrocarbon, usually methane. This process is represented by a cathedral oven provided with tubes containing a catalyst through which methane and steam flow to convert these reactants into CO and H₂, i.e. syngas. The purpose of the oven is to heat the tubes by heat radiation to reach the reaction temperatures up to 800°C. Syngas is then cooled down and separated down stream the oven. In alternative syngas is produced from coal gasification. The gasification reactor is fed with coal oxygen and steam to achieve a syngas stream by partial oxidation reaction of the coal itself. Nowadays gasification is technologically feasible also for biomasses and agricultural/industrial residues or solid urban waste, but substantially with the same finality to partially oxidize the reactants in order to obtain syngas.

SUMMARY OF THE INVENTION

The Applicant has found a process for producing synthesis gas (syngas) comprising the endothermic reaction between CO₂ and H₂S.

The energetic supply of this syngas production process is provided by the exothermic oxidation of a portion of H₂S to SO₂ according to the following reaction scheme:



This syngas production process is carried out according to the following overall theoretical reaction scheme R1, not taking into account the aforementioned R2 reaction



This process is further characterized in that the amount of fed oxygen is comprised between 5% and 25% by volume over the total volume of fed reactants gaseous mixture.

DESCRIPTION OF THE FIGURES

Figure 1 represents a block diagram of a thermal reactor used in the process of the invention.

Figure 2 represents a scheme of a regenerative thermal reactor utilized in the process of the invention in the presence of oxygen or air.

5 Figure 3 represents a block diagram of an independent productive unit to carry out the process of the invention.

Figure 4 represents a block diagram of a conventional Claus type productive unit for sulfur recovery.

10 Figure 5 represents a block diagram of a productive unit to carry out the process of the invention integrated with a Claus type catalytic train.

Figure 6 represents a block diagram of a conventional type productive unit for producing sulfuric acid

Figure 7 represents a block diagram of a productive unit for carrying out the process of the invention integrated with the productive unit for producing sulfuric acid.

15 Figure 8 represents a block diagram of a production unit for carrying out the process of the invention coupled with a production unit destined to methanol production.

Figure 9 represents a block diagram of a production unit for carrying out the process of the invention associated with a production unit for producing gasoline/gasoil according to Fischer Tropsch gas-to-liquids processes.

20 Figure 10 represents a block diagram of a production unit for carrying out the process of the invention coupled with a production unit for producing syngas from coal gasification.

DETAILED DESCRIPTION OF THE INVENTION

For the purposes of the invention the wording “overall theoretical reaction scheme” means the general and stoichiometric scheme of reactants conversion. This scheme and all
25 associated stoichiometry may vary according to the reactor methodologies as well the operating conditions thereof.

For the purposes of the present invention the definition “catalytic train of the Claus unit” means the series of catalytic converters and condensers for sulfur recovery that in Claus

unit are positioned downstream the thermal section.

For the purposes of the present invention the wording “oxygen” means pure oxygen, air, oxygen-enriched air, combustion air etc. Preferably oxygen is pure oxygen or air.

For the purposes of the present invention the wording “operating unit” means a plant for carrying out the process of the invention comprising a reactor at least one separation section, separating syngas from the other components of flue gases leaving said thermal or regenerative reactor, and least one recycling section of the unconverted reactants.

For the purposes of the present invention the wording “independent operating unit” means an operating unit to carry out the process according to the present invention, wherein the at least one separating section and/or at least one recycling section is apart from those of other operative units destined to different industrial processes.

For the purposes of the present invention for “small portion of H_2S ” it is intended the volume % of H_2S directly reacting with O_2 according to the aforementioned reaction R2, therefore (depending on the volume of O_2 entering the reactor) calculated on the total volume of fed H_2S .

For the purposes of the present invention the wording “efficient regeneration” means that the regenerative section of the reactor is able to significantly preheat the feed up to temperature close to the conditions of the thermal section of the reactor (i.e. over $1000^{\circ}C$).

I) PRODUCTION OF SYNGAS IN THE PRESENCE OF OXYGEN / AIR

The process of the invention is generally carried out by feeding oxygen/air in a reactor in amounts of from 5 to 25 % by volume mixture based on the total gaseous mixture sent to the reactor, in order to sustain energetically the syngas endothermic production via CO_2 reduction, preferably in the range of 5% to 15% when the regeneration is very efficient.

The process of the invention is carried out in a reactor, such as a regenerative thermal reactor or a thermal reactor, although the former is more preferred.

The regenerative thermal reactor (figure 2), in which syngas is produced, is preferably a tubular plug flow reactor (PFR) for the regenerative section and PFR for the thermal section internally covered with refractory and preferably provided downstream with a

waste heat boiler. According to a particularly preferred embodiment this reactor section is a thermal furnace covered with refractory and provided downstream with a waste heat boiler, in which medium/high pressure vapours are generated at the shell side by reactor flue gases that are cooled down entering the waste heat boiler at the tubes side.

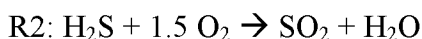
- 5 The regenerative thermal reactor preferably used in the process of the invention may have different configurations with reactants feed positioned in one or different reactor areas.

The process according to the present invention may also be carried out in a thermal reactor, that is a PFR, through which gases pass with a turbulent flow and provided downstream with a waste heat boiler, like that previously described.

- 10 The reaction temperatures of the process according to the present invention are preferably comprised between 800 and 1550°C.

More preferably the reaction temperatures are comprised between 1300 and 1550°C when a high sequestering therefore a high conversion of CO₂ and H₂S is required, whereas the process is carried out at lower temperatures (900-1100°C) when the target is to obtain a
15 relatively high H₂/CO ratio.

Fed oxygen sustains thermally the reaction R1 through the combustion of small part of H₂S according to the following reaction scheme:



- The exercise pressure is preferably comprised between 1 and 2 absolute atm., more
20 preferably between 1.5 and 2 atm.

The contact times are preferably between 0.1 and 3 s. more preferably between 0.5 and 1.5 s.

These parameters were obtained by carrying out a simulation we describe herein below only for illustrative but not limitative purposes.

- 25 The regenerative thermal reactor, or in alternative the thermal reactor used in the process according to the present invention is simulated by using complex kinetic schemes (Manenti et al., Multiscale modelling of Claus thermal furnace and waste heat boiler using detailed kinetics, Computers and Chemical Engineering, 59, 219-225, 2013), comprising 2426

chemical reactions and 142 chemical species. The simulation cannot be conducted by using commercial software, since the main processes simulators are not provided with complex kinetic schemes. Therefore the present simulation is carried out with the abovementioned tools previously in situ validated.

- 5 The thermal reactor is represented schematically in Figure 1. The simulation data are reported in the following table 1.

Table 1 Thermal reactor

DATA			
Temp in ¹	°C	250	250
Pressure	bar	1.5	1.5
CO ₂	kmol	10	10
H ₂ S	kmol	30	30
O ₂	kmol	11.81	5.79
RESULTS			
React. Temp. ²	°C	1500	1000
CO ₂	kmol	5.09	7.81
H ₂ S	kmol	3.58	18.29
S ₂	kmol	10.90	4.14
H ₂	kmol	5.37	3.67
CO	kmol	4.80	1.90
SO ₂	kmol	3.68	2.89
H ₂ O	kmol	20.86	7.97
COS	kmol	0.11	0.29

¹ Inlet Temperature

² Reactor Temperature

10

An alternative configuration of the reactor is the proposed regenerative (energetically integrated) thermal reactor and is schematically represented in Figure 2. The reactor receives CO₂ and H₂S reactant streams at a relatively low temperature (e.g. 250°C). This feedstock is preheated (e.g., up to 700°C) with flue gases leaving the furnace. Once the above temperature is reached, oxygen is fed to further increase the temperature up to the desired value (1300-1550°C). Flue gases are then cooled down, by exchanging heat with inlet gases. In this way a significant heat recovery is achieved, and the oxygen amount

15

required to sustain the production of syngas is decidedly lower than that required in the thermal reactor.

The simulation data for the regenerative reactor are reported in the following table 2.

Table 2. Regenerative reactor

5

DATA			
Temp. In ¹	°C	700	700
Pressure	bar	1.5	1.5
CO ₂	kmol	10	10
H ₂ S	kmol	30	30
O ₂	kmol	9.19	3.47
RESULTS			
React. Temp ²	°C	1500	1000
CO ₂	kmol	4.47	7.44
H ₂ S	kmol	4.32	19.79
S ₂	kmol	11.25	3.98
H ₂	kmol	6.32	3.99
CO	kmol	5.40	2.23
SO ₂	kmol	2.25	1.67
H ₂ O	kmol	19.16	6.16
COS	kmol	0.13	0.33

¹ Inlet temperature

² Reactor Temperature

Optimal conditions change at different operating conditions as reported hereinbelow for illustrative but not limitative purposes.

- 10 The following data are related to the proposed reaction conducted at 1300°C, 1.8 bar and 1 s residence time. Whenever the feedstock temperature is lower than the reaction temperature, additional O₂ is needed to increase the temperature itself.

CONDITION 1 - HIGH H₂S CONTENT

T = 1300 °C P = 1.8 bar Residence time = 1 s

- 15 Molar Fraction Inlet: 82% H₂S, 10% CO₂, 8% O₂

Output: 24.4%v syngas, H₂/CO Ratio = 3, no production of SO₂, conversion of H₂S = 60%v and CO₂ = 70%v

Since no SO_2 is generated, there is a high selectivity towards H_2 and the process is not necessary to be associated with plants directed to exhaust SO_2 like for example that occurring in the Claus catalytic train or in the sulphuric acid production as reported later on.

5 **CONDITION 2 - HIGH CO_2 CONTENT**

$T = 1300^\circ\text{C}$ $P = 1.8 \text{ bar}$ Residence time = 1 s

Molar Fraction Inlet: 31% H_2S , 62% CO_2 , 7% O_2

Output: H_2/CO Ratio = 0.2, $\text{H}_2\text{S}/\text{SO}_2$ Ratio = 1, Conversion of $\text{H}_2\text{S} = 87\%v$ and $\text{CO}_2 = 35.5\%v$

- 10 Production of SO_2 : possibility to couple it, for instance, with Claus catalytic converters and/or sulfuric acid plants as reported later on.

Oxygen quantity is less due to the amount of CO_2 that works as Oxygen basin for H_2S oxidation.

CONDITION 3 - OPTIMAL CLAUS CATALYTIC CONVERTER MATCHING

- 15 $T = 1300^\circ\text{C}$ $P = 1.8 \text{ bar}$ Residence time = 1 s

Molar Fraction Inlet: 40% H_2S , 52% CO_2 , 8% O_2

Output: $\text{H}_2\text{S}/\text{CO}_2$ Ratio = 2 (Claus optimal condition), Conversion of $\text{H}_2\text{S} = 85\%v$ and $\text{CO}_2 = 40\%v$, 21.5%v syngas, H_2/CO Ratio = 0.35

2. SEPARATION OF SYNGAS FROM OTHER REACTOR FLUE GASES

- 20 Flue gases coming from the reactor are cooled down and syngas is separated from the other compounds namely H_2S , CO_2 , SO_2 , H_2O and S_2 . For this purpose the process of the invention is preferably carried out in a productive unit that, besides the regenerative thermal reactor, it further comprises at least one of conversion/condensation/ compression sections allowing the separation of flue gases from said reactors. This separation can be
- 25 realized in different ways, depending on the use of the different streams that, besides

syngas, may be utilized industrially, and the production site, wherein the production unit for carrying out the process according to the invention is integrated with.

Herein below for illustrative but not limitative purposes are reported some preferred embodiments of productive units for conducting the process according to the present invention, said operating units being independent or integrated with operating units destined to other industrial processes.

In figure 3 a preferred embodiment is depicted of an independent productive unit used for carrying out the process according to the present invention.

At the inlet of the reactor, indicated with “**NEW**” in the figure, preferably a regenerative thermal reactor, acid gas (mainly H_2S), CO_2 and oxygen (O_2) or combustion air or other fuel mixture are fed. In the regenerative thermal reactor CO_2 reduction to CO occurs, with H_2 formation through H_2S pyrolysis, thereby producing syngas. S_2 , SO_2 and H_2O form as by products. Flue gases are cooled down in a waste heat boiler not represented in the figure. Cooling down must be sufficiently quick to avoid any recombination reactions among flue gases (Manenti et al., Design of SRU thermal reactor and waste heat boiler considering recombination reactions, *Procedia Engineering*, 42, 414-421, 2012). After cooling down, separation of elemental sulfur is performed in Sep.1 through condensation. Sulfur is then sent to sulfur pit and thereafter sold or used for other processes (e.g. for the preparation of sulfuric acid). The residual stream contains unreacted H_2S and CO_2 , SO_2 , H_2O and syngas. By subsequent treatments occurring separately in **Sep.2**, **Sep.3** and **Sep. 4** or occurring in the same separators combined among each other, it is possible to purify syngas. Before condensing water, sulfur vapours must be hydrogenated, to avoid that sulfur solidifies, thereby obstructing pipelines.

SO_2 can be used in sulfuric acid production processes. As syngas production is always associated with a compression thereof at different tens of atmospheres, no further operating cost is required if SO_2 condensation occurs by pressure increase. For example syngas is compressed up to 80 bar or more for methanol synthesis (Manenti et al., Considerations on the Steady-state Modeling of Methanol Synthesis Fixed-Bed Reactor, *Chemical*

Engineering Science, 66(2), 152-162, 2011).

Compression favours also the last separation phase of syngas from unconverted H₂S and CO₂ and optional other acid by products by conventional washing with (amine) solvent, able to sequester H₂S and CO₂ and release syngas. Sequestered H₂S and CO₂, once
5 recovered from the solvent are recycled at the reactor.

The process of the invention is able to exhaust and increase the values of two by products like H₂S and CO₂ having a strong environmental impact, thereby producing syngas with different CO/H₂ ratios; in addition the process of the invention, besides being energetically sustainable shows high conversion yields.

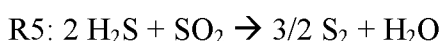
10 As above seen, the separations for the purification of syngas occur without additional compression costs if compared to conventional technologies of separation processes (amine washing), favouring therefore the insertion/integration of the process of the invention in conventional processes, as reported herein below.

1. Sulfur recovery unit with syngas coproduction

15 The process of the invention is particularly useful for increasing the performances and profits of sulfur recovery units. The typical scheme of a sulfur recovery unit is depicted in Figure 4. The acid gas to be treated is fed with non stoichiometric combustion air to a Claus furnace wherein part of H₂S is converted to SO₂ according to the following reaction.



20 The reaction is generally conducted at temperatures higher than 1000°C, with temperatures that may be higher than 1500°C in the presence of ammonia fractions in the acid gas stream. When leaving Claus furnace flue gas is cooled down to 300°C in a waste heat boiler with production of medium pressure vapor. A condenser downstream the waste heat boiler completes cool down by separating sulfur by condensation. Condensed sulfur is sent
25 to liquid sulfur pit. The stream, thus free from sulfur, mainly consisting of H₂S, SO₂ and H₂O enters the first Claus catalytic converter **CC1**, wherein the following reaction occurs:



This is an equilibrium reaction, requiring to be performed a multiple step process, with

intermediate thermal treatment and subsequent intermediate removal of the product (S_2). With 2-3 catalytic steps yields higher than 90% can be reached. Tail residue, usually contains a small percentage of unconverted H_2S (for example when molar ratios H_2S/SO_2 higher than 2 are present in flue gases leaving Claus furnace). This residue is then washed
5 with solvent for residual H_2S abatement. H_2S is then released from the stripper head and upstream recycled at Claus furnace feed, in addition to freshly fed acid gas.

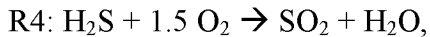
The process of the invention allows to use to the best the technology of conventional Claus process and producing syngas with decidedly low costs. A possible application is represented in Figure 5. Flue gases coming from syngas reactor **NEW** are sent to the
10 classic catalytic train converter of the Claus process (sulfur unit recovery) upstream or downstream the first condenser **Cond**.

After the first sulfur removal, the mixture containing CO_2 , H_2S , SO_2 , H_2O and syngas is fed at the catalytic train **CC1-CC2**, wherein the Claus reaction R5 occurs. Syngas is inert both on the catalytic bed (not titanium based catalyst) and in intermediate sulfur
15 condensing and removal operating conditions. Therefore flue gases coming from the third condenser **Cond** are unconverted CO_2 , H_2S and syngas. Syngas is recovered at the top of the amine washing column (**ABSORBER** in fig. 5), whereas H_2S and CO_2 are recovered at the top of the stripper (**STRIPPER** in the same figure) and recycled upstream the reactor. The operating unit to carry out the process of the invention integrated with Claus sulfur
20 recovery unit (in this specific example only with Claus catalytic train) allows to exhaust CO_2 by H_2S reduction, thereby coproducing syngas and elemental sulfur.

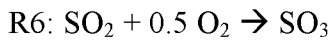
In figures 4 and 5 the hydrogenation reactor operating the sulfur vapours and sulfurated by products reduction and the quench tower performing cooling down of flue gases and process water condensation upstream the absorber are not reported.

25 2.Sulfuric acid production unit

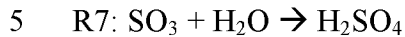
A production unit of sulfuric acid is schematically represented in Figure 6. In particular the production process encompasses the primary oxidation of sulfurated compounds, for example acid gas (H_2S) according to the above mentioned global reaction



The successive secondary oxidation of SO_2 :



and finally SO_3 absorption in water:



The process according to the present invention may be integrated with the aforementioned process. The insertion of an independent operating unit to carry out the process of the invention in a possible revamp is reported in Fig. 7. In this case the thermal furnace of direct oxidation of H_2S to SO_2 according to the aforementioned reaction R4 is replaced by
10 the reactor indicated with NEW in Figure 7, preferably a regenerative thermal reactor, wherein the process according to the present invention is carried out and from which SO_2 is in any case obtained.

The following advantages of this revamp are obtained: besides the sulfuric acid production, the revamp allows to obtain syngas associated with CO_2 abatement, which have a
15 considerable economic value.

Purification of natural gas

Natural gas is extracted by gases wells in the form of a gas or a volatile product released by liquid masses or porous solids. In any case it is a mixture of the so called light and volatile hydrocarbon compounds, in part defined as incondensable (i.e. methane) because of their
20 very low condensation temperature. Very often natural gas contains a more or less marked presence of H_2S and CO_2 according to the location of the specific deposit. For example Kashgan site in Kazakhstan, one of the world largest gas natural deposit, has an elevated amount of H_2S (about 20% on the total natural gas content). Therefore the need is felt to purify natural gases from CO_2 and H_2S and the most known technology to remove these
25 contaminants is the amine sweetening (washing) previously mentioned.

Once separated from natural gas, these compounds are often re-injected in the deposits because of the impossibility of a removal thereof. The process of the invention is particularly attractive for sequestering and converting CO_2 and H_2S coming also from

different streams and processes, thereby producing syngas as well as elemental sulfur in case the invention is integrated with sulfur recovery units. The process of the invention is even more attractive in case the deposits are already provided with amine washing columns, which the reactor, preferably a regenerative thermal reactor, to carry out the process according to the present invention may be connected to.

4. Production unit integrated in a production unit for producing methanol.

The invention allows to produce syngas for methanol synthesis occurring according to the overall reaction (Manenti et al., Considerations on the Steady-state Modeling of Methanol Synthesis Fixed-Bed Reactor, Chemical Engineering Science, 66(2), 152-162, 2011):



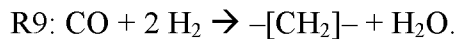
This synthesis requires elevated pressures (from 80 bar on) and H_2/CO ratios higher than 2 (preferably higher than 3-4) to obtain yields of 6-7% (yields of the industrial processes). An independent operating unit comprising a reactor, preferably a regenerative thermal reactor, to carry out the process according to the present invention allows to obtain syngas to be used in methanol production.

Figure 8 reports a scheme of an operating unit for example to produce methanol according to Lurgi, Casale and Davy Process Technology (Manenti et al., Considerations on the Steady-state Modeling of Methanol Synthesis Fixed-Bed Reactor, Chemical Engineering Science, 66(2), 152-162, 2011). In the synthesis reaction of methanol also CO_2 is involved (reverse water gas shift reaction), that, together with unconverted syngas, may be recycled upward the methanol reactor and/or the reactor, indicated with “NEW” in the figure, to carry out of the process of the invention, preferably a regenerative thermal reactor.

An alternative operating unit to carry out the process of the invention integrated with Claus operating unit may be also encompassed to be associated with a methanol plant production.

5. Gas to liquid production of gasolines and gasoils

Syngas is the starting reactant of Fischer Tropsch gas-to-liquid processes. In these processes, syngas is transformed into hydrocarbon compounds with progressively longer chains (indicated with the single unit $-\text{[CH}_2\text{]}-$ according to the overall reaction:



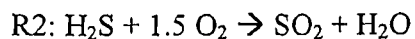
Therefore syngas prepared with the process according to the present invention in the reactor **NEW** and purified by passing it through the 4 separation sections **Sep1-Sep4** may be used as starting reactant in the Fischer Tropsch gas-to-liquid process as reported in Figure 9.

Coal Gasification

The process of the invention allows to obtain syngas as a support for coal gasification according to what reported in Figure 10. Coal gasification reactor receives coal, steam and oxygen as reactants to produce syngas. Gasification by products are CO_2 and H_2S (due to the presence of sulfur in loaded coal) and may be fed at the reactor **NEW**, **preferably a regenerative thermal reactor**, wherein the process according to the present invention is carried out, thereby increasing coal syngas production.

CLAIMS

1. A process for producing synthesis gas (syngas) comprising the endothermic reaction between CO₂ and H₂S, wherein the energetic supply is provided by the exothermic oxidation of a portion of H₂S to SO₂ according to the following reaction scheme:



said process being carried out according to the following overall theoretical reaction scheme R1, not taking into account the aforementioned exothermic reaction R2,



wherein the amount of fed oxygen is comprised between 5% and 25% by volume over the total volume of fed reactants gaseous mixture.

2. The process according to claim 1 wherein the amount of fed oxygen is comprised between 5% and 15%, when regeneration is very effective.

3. The process according to any one of claims 1 or 2, wherein the reaction temperature is comprised between 850 and 1550°C for residence times comprised between 0.1s and 3s.

4. The process according to claim 3, wherein said temperature reaction is comprised between 1300 and 1550°C to obtain the maximum conversion of CO₂ and H₂S.

5. The process according to claim 3 wherein the temperature reaction is comprised between 850°C and 1100°C to obtain a synthesis gas with higher H₂/CO ratios.

6. The process according to anyone of claims 1 to 5, being carried out in a production unit comprising:

- a reactor (NEW),
- at least one separation section (Sep.1-Sep4, CC1-CC2, COND, ABSORBER, STRIPPER) of the various components of the gaseous mixture leaving said thermal/regenerative reactor, and
- at least one section for recycling the unconverted H₂S and CO₂.

7. The process according to claim 6, wherein said reactor (NEW) is a regenerative thermal flow reactor or a thermal reactor.

8. The process according to claim 7, wherein said regenerative thermal flow reactor comprises:

a) a regenerative section being a tubular PFR, in which fed gases are preheated and through which gases pass with a turbulent flow

5 b) a thermal section, being a PFR, in which the reactions R1 and R2 take place and through which gases pass with a turbulent flow,

said regenerative thermal reactor being optionally provided downstream with a waste heat boiler.

9. The process according to claim 7 wherein said thermal reactor is a PFR, through which
10 gases pass with a turbulent flow.

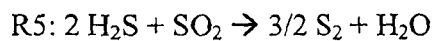
10. The process according to any one of claims 8 and 9 wherein said waste heat boiler receives the gases leaving the reactor and said gases cool down at the tube side while generating medium-high pressure vapours at the shell side.

11. The process according to anyone of claims 6-10, wherein the effluent of the reactor is
15 purified in a separation section that comprises:

- a first separation section (**Sep.1**) wherein sulfur is separated by cooling from the gaseous mixture and collected in a suitable tank;
- a second separation section (**Sep.2**) wherein the gaseous mixture leaving said first separation section (**Sep.1**) and comprising CO, H₂, H₂O, SO₂ and CO₂ and
20 unconverted H₂S and possibly nitrogen, in case the process is carried out in the presence of air, is cooled down to allow the separation of water by condensation,
- a possible third separation section (**Sep.3**), wherein SO₂ is separated from the gaseous mixture by washing or chemical conversion,
- a fourth separation section (**Sep. 4**) wherein the mixture leaving said third
25 separation section (**Sep. 3**) and comprising H₂S, CO₂, CO and H₂ is washed to separate the synthesis gas from the reactants not yet converted, which are recovered and then recycled at the reactor,

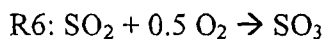
said separation sections being able to be combined or integrated with one another.

12. The process according to anyone of claims 6-10, wherein the gases entering the reactor (NEW) are H₂S, O₂ or air and CO₂ and wherein the gases leaving said reactor are cooled in a boiler for steam recovery (WASTE HEAT BOILER) and then sent to a first condenser (Cond) of a Claus unit for sulfur recovery, in a sulfur pit (SULFUR PIT), whereas the
5 gases leaving said condenser are sent to a catalytic conversion section, where the following reaction takes place:

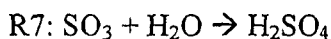


said catalytic conversion section comprising at least 1 catalytic converter (CC1) and (CC2) arranged in succession and spaced by at least 1 condenser (Cond) to allow the partial
10 recovery of sulfur, formed in each converter, said sulfur being conveyed into the aforementioned sulfur pit, and the gaseous mixture leaving the last condenser (Cond) of said catalytic conversion section and comprising CO, H₂, CO₂, H₂S, and possibly nitrogen pass through a hydrogenation reactor and a quenching tower, and then to a solvent washing column (ABSORBER), wherein said gaseous mixture is washed with amines to recover
15 the unconverted CO₂ and H₂S at the top of a stripper (STRIPPER) and recycled at the thermal/regenerative reactor (NEW), whereas the synthesis gas is recovered at the top of said solvent washing column.

13. The process according to any one of claims 6-11, wherein SO₂ coming from the third separation section (Sep. 3) is sent to a reactor R7 where the following reaction is carried
20 out



and SO₃ thus formed and leaving the reactor R7 is reacted in the presence of water in the reactor R8 to give sulfuric acid according to the following reaction scheme:



14. The process according to anyone of claims 6-11, wherein syngas leaving the fourth separation section (Sep 4) is conveyed to a production unit for producing methanol.

15. The process according to anyone of claims 6-11, wherein the reactants CO₂ and H₂S come from natural gas deposits.

16. The process according to claim anyone of claims 6-11, wherein syngas leaving the fourth separation section (**Sep 4**) is sent to a production unit for producing gasoline and gasoil through the gas-to-liquid Fischer Tropsch process.

17 The process according to anyone of claims 6-11, wherein the reactants CO₂ and H₂S
5 come totally or in part from a coal gasification unit.

Figure 1

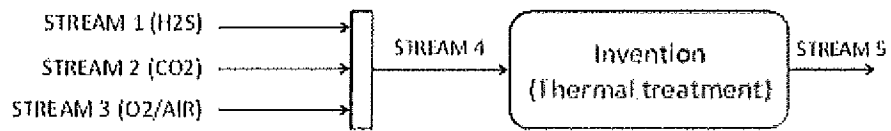


Figure 2

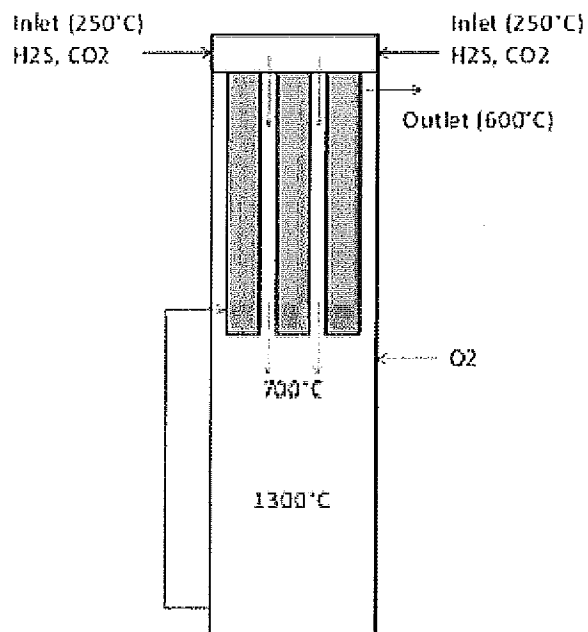


Figure 3

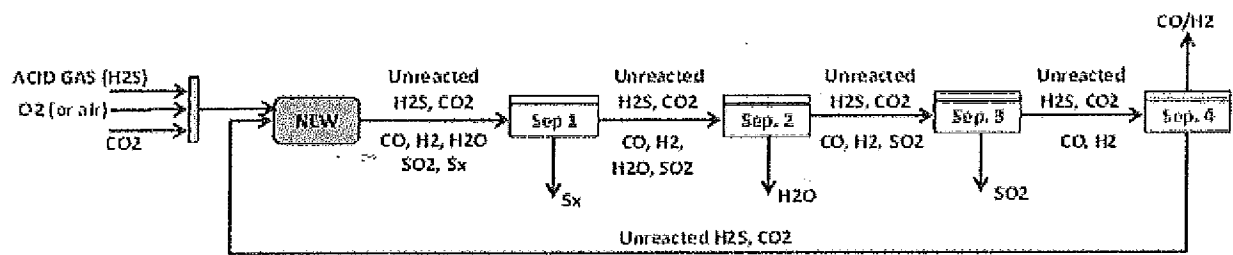


Figure 4

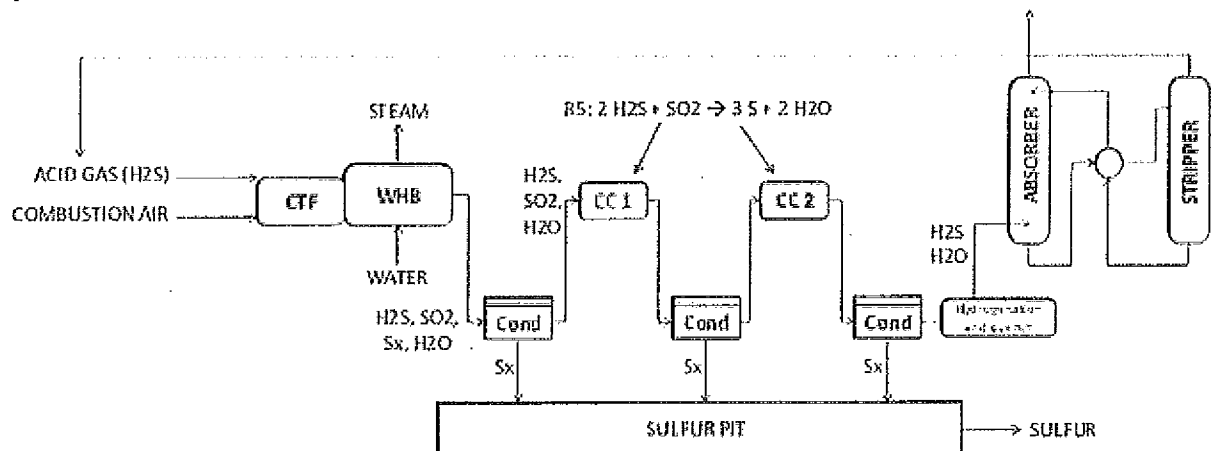


Figure 5

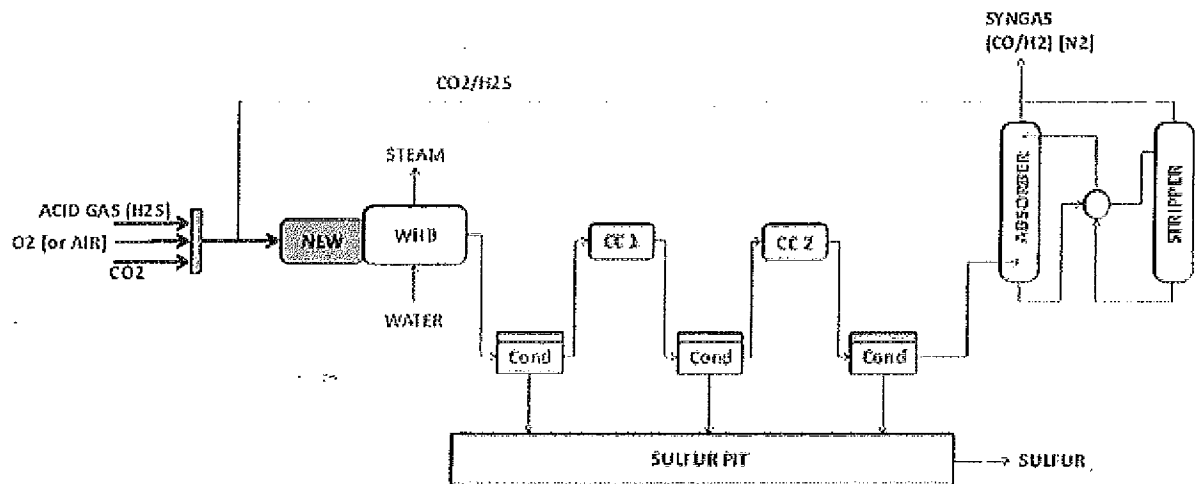


Figure 6

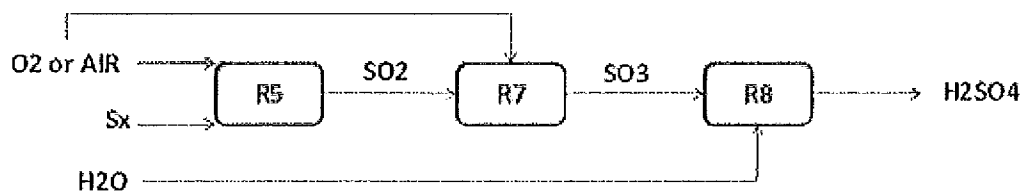


Figure 7

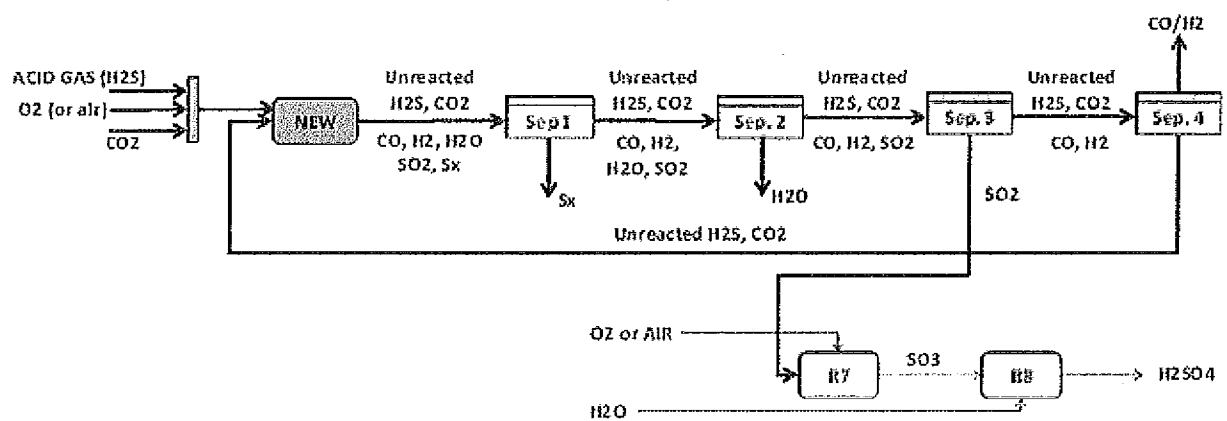


Figure 8

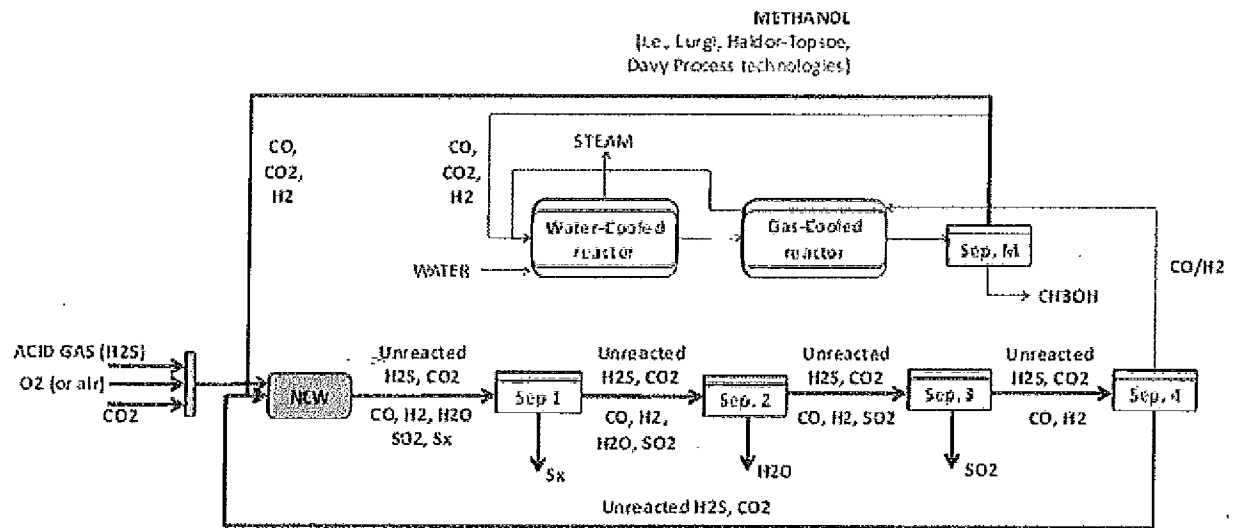


Figure 9

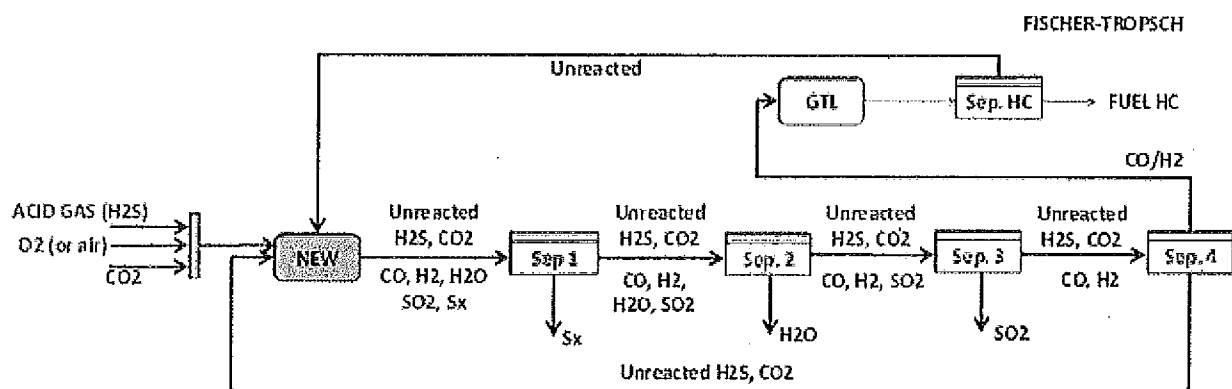
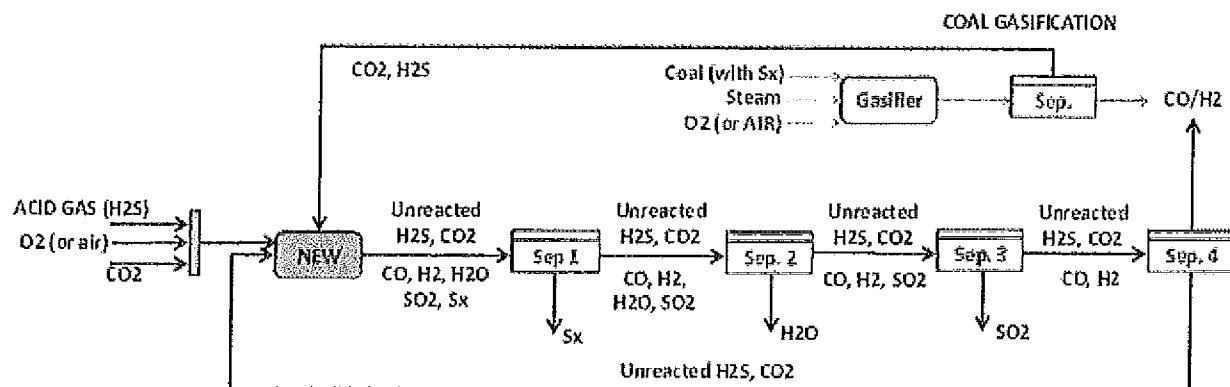


Fig.10



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063593

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/06 C01B17/04 C01B17/50
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, CHEM ABS Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 999 178 A (BOWMAN MELVIN G [US]) 12 March 1991 (1991-03-12) tables ----- -/--	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

31 October 2014

Date of mailing of the international search report

11/11/2014

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Authorized officer

Engelen, Karen

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063593

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GAVIN P. TOWLER ET AL: "Development of a zero-emissions sulfur-recovery process. 1. Thermochemistry and reaction kinetics of mixtures of hydrogen sulfide and carbon dioxide at high temperature", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 32, no. 11, 1 November 1993 (1993-11-01), pages 2800-2811, XP055108551, ISSN: 0888-5885, DOI: 10.1021/ie00023a050 the whole document -----	1-17
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International application No

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