(19) DANMARK

(10) DK/EP 3027552 T3

Patent- og Varemærkestyrelsen

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: *C 01 B 3/06 (2006.01)* *C 01 B 17/04 (2006.01)* *C 01 B 17/50 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2019-11-25**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2019-08-28**

(86) Europæisk ansøgning nr.: **14777817.9**

(86) Europæisk indleveringsdag: **2014-07-31**

(87) Den europæiske ansøgnings publiceringsdag: **2016-06-08**

(86) International ansøgning nr.: **IB2014063593**

(87) Internationalt publikationsnr.: **WO2015015457**

(30) Prioritet: **2013-08-02 IT MI20131322**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italien**

(72) Opfinder: **MANENTI, Flavio, c/o POLITECNICO DI MILANO, Piazza Leonardo da Vinci 32, I-20133 Milano, Italien**
PIERUCCI, Sauro, c/o POLITECNICO DI MILANO, Piazza Leonardo da Vinci 32, I-20133 Milano, Italien
MOLINARI, Lucio, Via Tonale 24, I-20125 Milano, Italien

(74) Fuldmægtig i Danmark: **Plougmann Vingtoft A/S, Strandvejen 70, 2900 Hellerup, Danmark**

(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF SYNGAS VED CO2-REDUKTION**

(56) Fremdragne publikationer:
GB-A- 2 143 225
US-A- 4 171 347
US-A- 4 999 178
PETER D. CLARK ET AL: "Comments on the Role of H2S in the Chemistry of Earth's Early Atmosphere and in Prebiotic Synthesis", JOURNAL OF MOLECULAR EVOLUTION, vol. 47, no. 2, 1 August 1998 (1998-08-01) , pages 127-132, XP055108881, ISSN: 0022-2844, DOI: 10.1007/PL00006369
GAVIN P. TOWLER ET AL: "Development of a zero-emissions sulfur-recovery process. 2. Sulfur-recovery process based on the reactions of hydrogen sulfide and carbon dioxide at high temperature", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 32, no. 11, 1 November 1993 (1993-11-01), pages 2812-2819, XP055108457, ISSN: 0888-5885, DOI: 10.1021/ie00023a051
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
TOWLER G ET AL: "DEVELOPMENT OF A ZERO-EMISSIONS SULPHUR-RECOVERY PROCESS", ICHEME RESEARCH EVENT, XX, XX, 1 January 1994 (1994-01-01), page 333/334, XP000749477,

Fortsættes ...

DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention relates a production process of synthesis gas starting from CO_2 and H_2S, said reactants being generated by industrial conventional processes or separated by conventional industrial purification processes.

BACKGROUND OF THE INVENTION

[0002] 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 H_2, 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.

[0003] Peter D. Clark et al in "Comments on the role of H2S in the Chemistry of Earth 's early atmosphere and in prebiotic Synthesis" Journal of Molecular Evolution vo. 47, No. 2, 1 August 1998, pages 127-132 discloses a small scale lab process for producing syngas starting from H2S and CO2 wherein the energetic supply for carrying out this reaction is supplied by an electrically heated surface.

[0004] US 4171347 describes a for the catalytic oxidation of H_2S to SO_2 in the presence of an oxidation catalyst like V_2O_5 or V_2S_5 at temperatures of from 150 to 482°C.

[0005] GB2143225 discloses only an improved Claus process carried out with specific catalysts comprising at least one metal selected Group 3b and/or 4b of the periodic table of the elements on a silica containing carrier .

SUMMARY OF THE INVENTION

[0006] The applicant has found a process as claimed in claim 1 for producing synthesis gas.

DESCRIPTION OF THE FIGURES

[0007]

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.

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.

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.

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.

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

[0008] 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 associated stoichiometry may vary according to the reactor methodologies as well the operating conditions thereof.

[0009] 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.

[0010] 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.

[0011] 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.

[0012] 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.

[0013] 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.

[0014] 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°C).

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

[0015] 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.

[0016] The process of the invention is carried out in a regenerative flow reactor or a thermal reactor, although the former is more preferred.

[0017] 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.

[0018] 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.

[0019] The reaction temperatures of the process according to the present invention are comprised between 800 and 1550°C.

[0020] Preferably the reaction temperatures are comprised between 1300 and 1550°C when a high sequestering therefore a high conversion of CO_2 and H_2S is required, whereas the process is carried out at lower temperatures (900-1100°C) when the target is to obtain a relatively high H_2/CO ratio.

[0021] Fed oxygen sustains thermally the reaction R1 through the combustion of small part of H_2S according to the following reaction scheme:

R2: $H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$

[0022] The exercise pressure is preferably comprised between 1 and 2 absolute atm., more preferably between 1.5 and 2 atm.

[0023] The contact times are preferably between 0.1 and 3 s. more preferably between 0.5 and 1.5 s.

[0024] These parameters were obtained by carrying out a simulation we describe herein below only for illustrative but not limitative purposes.

[0025] 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.

[0026] 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

DATA			
Pressure	bar	1.5	1.5
CO_2	kmol	10	10
H_2S	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_2S	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_2O	kmol	20.86	7.97
COS	kmol	0.11	0.29
[1] Inlet Temperature [2] Reactor Temperature			

[0027] An alternative configuration of the reactor is the proposed regenerative (energetically integrated) thermal reactor and is schematically represented in Figure 2. The reactor receives CO_2 and H_2S 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 required to sustain the production of syngas is decidedly lower than that required in the thermal reactor.

[0028] The simulation data for the regenerative reactor are reported in the following table 2.

Table 2. Regenerative reactor

DATA			
Temp. In [1]	°C	700	700
Pressure	bar	1.5	1.5
CO_2	kmol	10	10
H_2S	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_2S	kmol	4.32	19.79
S_2	kmol	11.25	3.98
H2	kmol	6.32	3.99
CO	kmol	5.40	2.23
SO_2	kmol	2.25	1.67
H_2O	kmol	19.16	6.16
COS	kmol	0.13	0.33
[1] Inlet temperature [2] Reactor Temperature			

[0029] Optimal conditions change at different operating conditions as reported hereinbelow for illustrative but not limitative purposes.

[0030] 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 O_2 is needed to increase the temperature itself.

CONDITION 1 - HIGH H_2S CONTENT

[0031]

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

Molar Fraction Inlet: 82% H_2S, 10% CO_2, 8% O_2

Output: 24.4%v syngas, H_2/CO Ratio = 3, no production of SO_2, conversion of H_2S = 60%v and CO_2 = 70%v

[0032] 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.

CONDITION 2 - HIGH CO_2 CONTENT

[0033]

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

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

Output: H_2/CO Ratio = 0.2, H_2S/SO_2 Ratio = 1, Conversion of H_2S = 87%v and CO_2 = 35.5%v

[0034] Production of SO2: possibility to couple it, for instance, with Claus catalytic converters and/or sulfuric acid plants as reported later on.

[0035] Oxygen quantity is less due to the amount of CO2 that works as Oxygen basin for H2S oxidation.

CONDITION 3 - OPTIMAL CLAUS CATALYTIC CONVERTER MATCHING

[0036]

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

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

Output: H_2S/CO_2 Ratio = 2 (Claus optimal condition), Conversion of H_2S = 85%v and CO_2 = 40%v, 21.5%v syngas, H_2/CO Ratio = 0.35

2. SEPARATION OF SYNGAS FROM OTHER REACTOR FLUE GASES

[0037] 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 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.

[0038] 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.

[0039] In figure 3 a preferred embodiment is depicted of an independent productive unit used for carrying out the process according to the present invention.

[0040] 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.

[0041] 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).

[0042] Compression favours also the last separation phase of syngas from unconverted H_2S and CO_2 and optional other acid by products by conventional washing with (amine) solvent, able to sequester H_2S and CO_2 and release syngas. Sequestered H_2S and CO_2, once recovered from the solvent are recycled at the reactor.

[0043] The process of the invention is able to exhaust and increase the values of two by products like H_2S and CO_2 having a strong environmental impact, thereby producing syngas with different CO/H_2 ratios; in addition the process of the invention, besides being energetically sustainable shows high conversion yields.

[0044] 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

[0045] 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 H_2S is converted to SO_2 according to the following reaction.

R4: $H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O$

[0046] 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 to liquid sulfur pit. The stream, thus free from sulfur, mainly consisting of H_2S, SO_2 and H_2O enters the first Claus catalytic converter **CC1,** wherein the following reaction occurs:

R5: $2\ H_2S + SO_2 \rightarrow 3/2S_2 + H_2O$

[0047] 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 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.

[0048] 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 classic catalytic train converter of the Claus process (sulfur unit recovery) upstream or downstream the first condenser **Cond.**

[0049] 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 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 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.

[0050] 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.

2. Sulfuric acid production unit

[0051] 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

R4: $H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$,

[0052] The successive secondary oxidation of SO_2:

R6: $SO_2 + 0.5O_2 \rightarrow SO_3$

and finally SO_3 absorption in water:

R7: $SO_3 + H_2O \rightarrow H_2SO_4$

[0053] 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 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.

[0054] 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 considerable economic value.

Purification of natural gas

[0055] 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 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 contaminants is the amine sweetening (washing) previously mentioned.

[0056] 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.

[0057] 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):

R8: $CO + 2\ H_2 \rightarrow CH_3OH$

[0058] 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.

[0059] 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.

[0060] 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

[0061] 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 -[CH_2]- according to the overall reaction:

R9: $CO + 2\ H_2 \rightarrow -[CH_2]- + H_2O$.

[0062] 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

[0063] 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.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in

compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US4171347A [0004]
- GB2143225A [0005]

Non-patent literature cited in the description

- **PETER D. CLARK et al.**Comments on the role of H2S in the Chemistry of Earth 's early atmosphere and in prebiotic SynthesisJournal of Molecular Evolution, 1998, vol. 47, 2127-132 [0003]
- **MANENTI et al.**Multiscale modelling of Claus thermal furnace and waste heat boiler using detailed kineticsComputers and Chemical Engineering, 2013, vol. 59, 219-225 [0025]
- **MANENTI et al.**Design of SRU thermal reactor and waste heat boiler considering recombination reactionsProcedia Engineering, 2012, vol. 42, 414-421 [0040]
- **MANENTI et al.**Considerations on the Steady-state Modeling of Methanol Synthesis Fixed-Bed ReactorChemical Engineering Science, 2011, vol. 66, 2152-162 [0041] [0057] [0059]

Patentkrav

1. Fremgangsmåde til at fremstille syntesegas omfattende den endotermiske reaktion mellem CO_2 og H_2S, ifølge det følgende overordnede teoretiske reaktionsskema

R1: $CO_2 + 2\ H_2S \rightarrow CO + H_2 + S_2 + H_2O$; hvor:

i) energiforsyningen tilvejebringes ved den exotermiske oxidering af en del af H_2S til SO_2 ifølge det følgende reaktionsskema:

R2: $H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O$

ii) mængden af tilført oxygen til at udføre R2 er omfattet mellem 5 og 25 volumenprocent over det samlede volumen af gasformig blanding af tilførte reaktanter;

iii) nævnte fremgangsmåde udføres ved en temperature omfattet mellem 800 og 1550°C

i en produktionsenhed omfattende:

- en regenerativ termisk strømningsreaktor eller en termisk reaktor **(NY),**
- mindst et adskillelsesafsnit **(Sep.1-Sep4, CC1-CC2, COND, ABSORBER, STRIPPER)** af de forskellige komponenter af den gasformige blanding, der forlader nævnte termiske reaktor eller regenerative termiske strømningsreaktor, og
- mindst et afsnit til at genanvende det ikke-omdannede H_2S og CO_2.

2. Fremgangsmåde ifølge krav 1, hvor mængden af tilført oxygen er omfattet mellem 5% og 15%, når regeneration er meget effektivt.

3. Fremgangsmåde ifølge et hvilket som helst af kravene 1 eller 2, hvor reaktionstemperaturen er omfattet mellem 850 og 1550°C for opholdstider omfattet mellem 0,1s og 3s.

4. Fremgangsmåde ifølge krav 3, hvor nævnte temperaturreaktion er omfattet mellem 1300 og 1550°C for at opnå den maksimale omdannelse af CO_2 og H_2S.

5. Fremgangsmåde ifølge krav 3, hvor temperaturreaktionen er omfattet mellem 850°C og 1100°C for at opnå en syntesegas med højere H_2/CO-forhold.

6. Fremgangsmåde ifølge et hvilket som helst af kravene 1-5, hvor nævnte regenerative termiske strømningsreaktor omfatter:

a) et regenerativt afsnit, der er en tubulær PFR, hvori tilførte gasser forvarmes og hvorigennem gasser passerer med en turbulent strømning

b) et termisk afsnit, som er en PFR, hvori reaktionerne R1 og R2 finder sted, og hvorigennem gasser passerer med en turbulent strømning,

idet nævnte regenerative termiske reaktor eventuelt er tilvejebragt nedstrøms med en spildvarmekedel.

7. Fremgangsmåde ifølge et hvilket som helst af kravene 1-5, hvor, nævnte termiske reaktor er en PFR, hvorigennem gasser passerer i en turbulent strømning.

8. Fremgangsmåde ifølge krav 6, hvor nævnte spildvarmekedel modtager gasserne, der forlader reaktoren, og nævnte gasser nedkøler ved rørsiden, idet der genereres middel- og højtryksdampe ved skalsiden.

9. Fremgangsmåde ifølge et hvilket som helst af kravene 1-8, hvor afløbet fra reaktoren oprenses i et adskillelsesafsnit, der omfatter:

- et første adskillelsesafsnit **(Sep.1)** hvor svovl adskilles fra den gasformige blanding ved afkøling og opsamles i en egnet tank;
- et andet adskillelsesafsnit **(Sep.2)** hvor den gasformige blanding, der forlader nævnte første adskillelsesafsnit **(Sep.1)** og omfatter CO, H_2, H_2O, SO_2 og CO_2 og ikke-omdannet H_2S og eventuelt nitrogen, i tilfælde af, at fremgangsmåden udføres i tilstedeværelsen af luft, afkøles for at tillade adskillelsen af vand ved kondensering,
- et muligt tredje adskillelsesafsnit **(Sep.3),** hvor SO_2 adskilles fra den gasformige blanding ved vask eller kemisk omdannelse,
- et fjerde adskillelsesafsnit **(Sep. 4)** hvor blandingen, der forlader nævnte tredje adskillelsesafsnit **(Sep. 3)** og omfatter H_2S, CO_2, CO og H_2 vaskes for at adskille syntesegassen fra de endnu ikke omdannede reaktanter, som genvindes og derefter genanvendes ved reaktoren,

idet nævnte adskillelsesafsnit er i stand til at blive kombineret eller integreret med hinanden.

10. Fremgangsmåde ifølge et hvilket som helst af kravene 1-8 hvor gasserne, der indføres i reaktoren **(NY)** er H_2S, O_2 eller luft og CO_2, og hvor gasserne, der forlader nævnte reaktor afkøles i en dampgenvindingskedel **(SPILDVARMEKEDEL)** og derefter tilføres til en første kondensator **(Cond)** af en Claus-enhed til svovlgenvinding, i en svovlgrav **(SVOVLGRAV),** hvorimod gasserne, der forlader nævnte kondensator, tilføres til et katalytisk omdannelsesafsnit, hvor den følgende reaktion finder sted:

R5: $2H_2S + SO_2 \rightarrow 3/2S_2 + H_2O$

idet nævnte katalytiske omdannelsesafsnit omfattende mindst 1 katalytisk omformer **(CC1)** og **(CC2)** anbragt efterfølgende hinanden og adskilt af mindst 1 kondensator **(Cond)** for at tillade den delvise genvinding af svovl, dannet i hver omformer, idet nævnte svovl transporteres ind i førnævnte svovlgrav, og den gasformige blanding, der forlader den sidste kondensator **(Cond)** af nævnte katalytiske omdannelsesafsnit og omfatter CO, H_2, CO_2, H_2S, og eventuelt nitrogen, passerer gennem en hydrogeneringsreaktor og et bratkølingstårn, og derefter til en opløsningsmiddel-vaskesøjle **(ABSORBER),** hvor nævnte gasformige blanding vaskes med aminer for at genvinde det ikke-omdannede CO_2 og H_2S oven på en gasstripper **(STRIPPER)** og genanvendes ved den termiske/regenerative reaktor **(NEW),** hvorimod syntesegassen genvindes oven på nævnte opløsningsmiddel-vaskesøjle.

11. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, hvor SO_2, der kommer fra det tredje adskillelsesafsnit **(Sep. 3)** tilføres til en reaktor R7, hvor den følgende reaktion udføres

R6: $SO_2 + 0.5O_2 \rightarrow SO_3$

og den dermed dannede SO_3, der forlader reaktoren R7, omdannes i tilstedeværelsen af vand i reaktoren R8 for at give svovlsyre ifølge det følgende reaktionsskema:

R7: $SO_3 + H_2O \rightarrow H_2SO_4$

12. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, hvor syngas, der forlader det fjerde adskillelsesafsnit **(Sep 4)**, transporteres til en produktionsenhed til fremstilling af methanol.

13. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, hvor reaktanterne CO_2 og H_2S kommer fra naturgasaflejringer.

14. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, hvor syngas, der forlader det fjerde adskillelsesafsnit **(Sep 4)**, tilføres til en produktionsenhed til fremstilling af benzin og diesel gennem gas-til-væske Fischer Tropsch-processen.

15. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, hvor reaktanterne CO_2 og H_2S kommer helt eller delvist fra en kulforgasningsenhed.

DRAWINGS

Figure 1

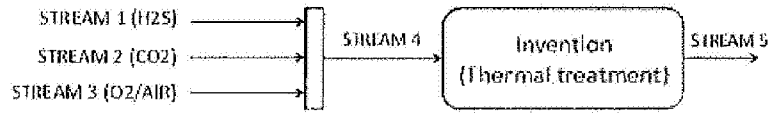


Figure 2

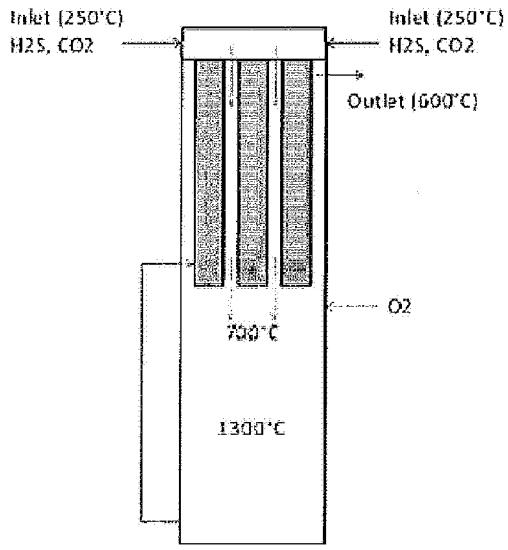


Figure 3

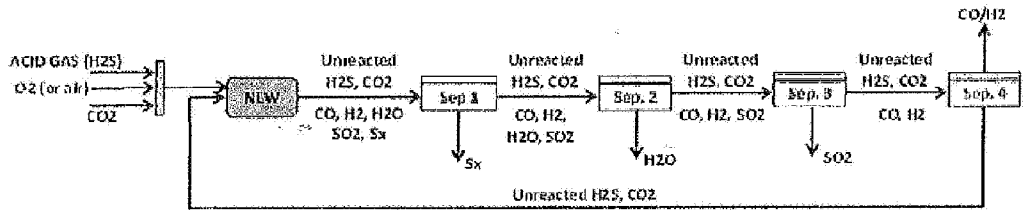


Figure 4

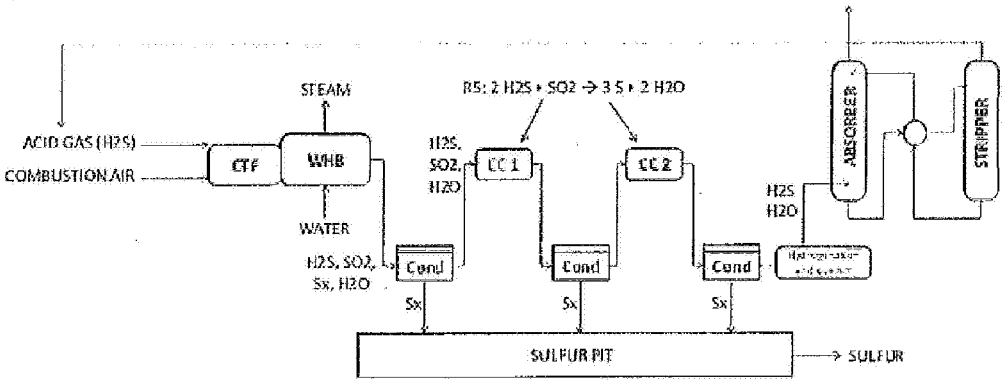


Figure 5

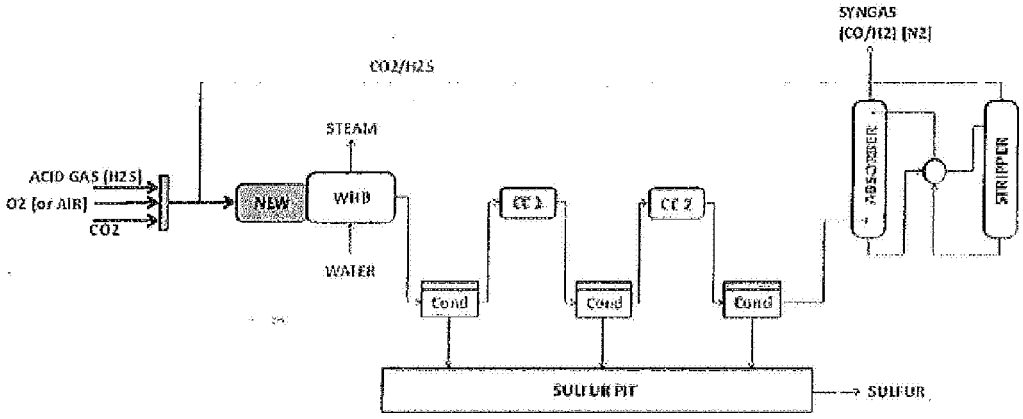


Figure 6

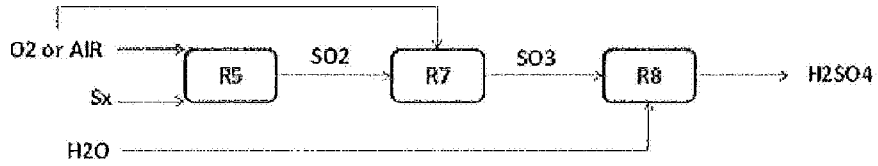


Figure 7

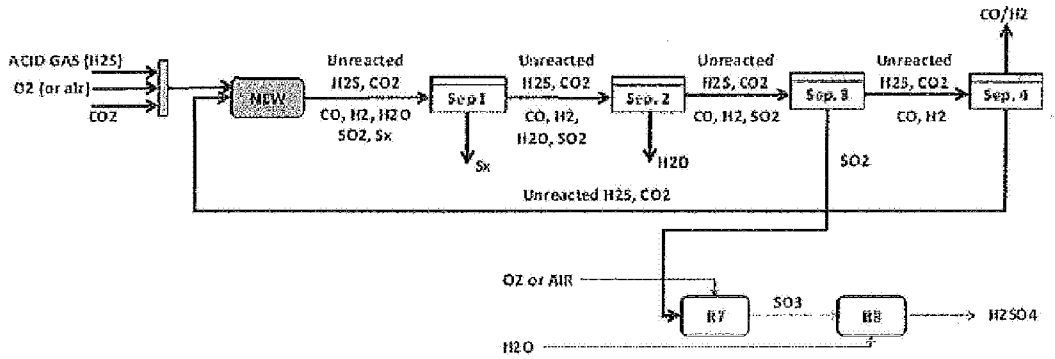


Figure 8

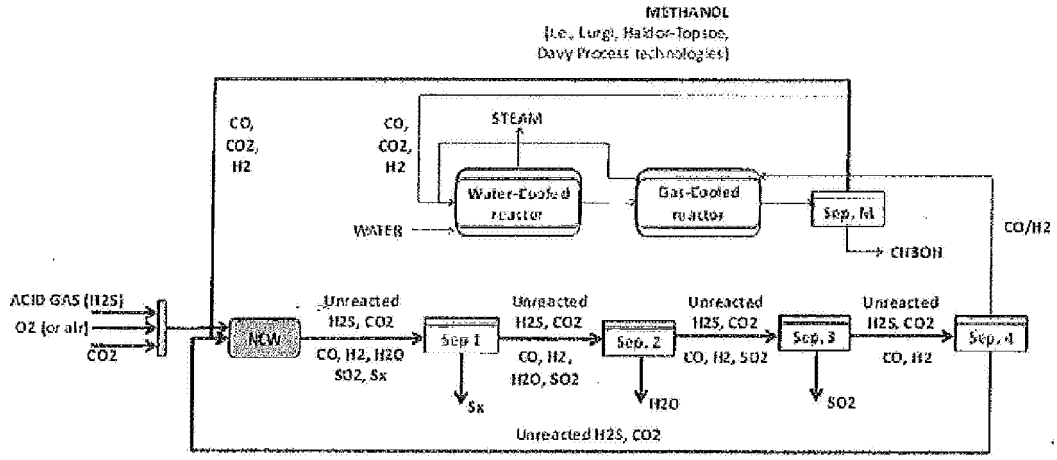


Figure 9

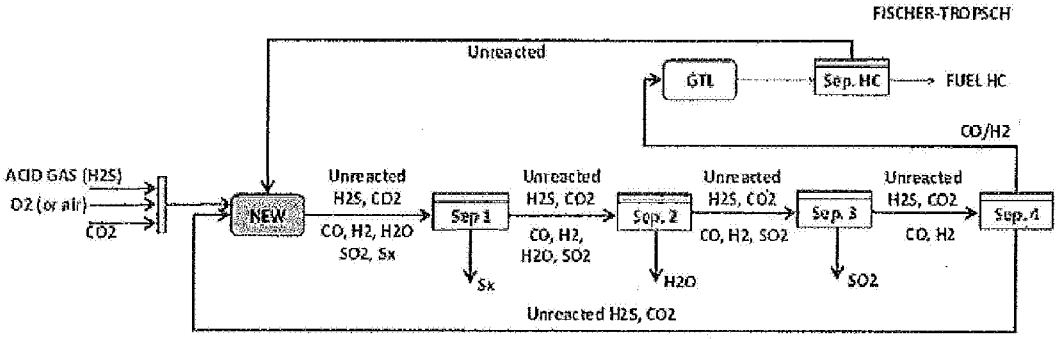
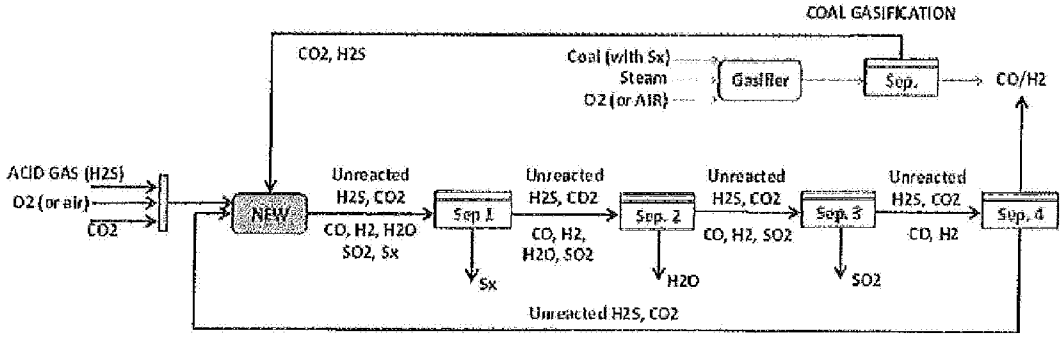


Fig.10


COAL GASIFICATION
CO2, H2S
Coal (with Sx)
Steam
O2 (or AIR)
Gasifier
Sep.
CO/H2
ACID GAS (H2S)
O2 (or air)
CO2
NEW
Unreacted
H2S, CO2
CO, H2, H2O
SO2, Sx
Sep 1
Sx
Unreacted
H2S, CO2
CO, H2,
H2O, SO2
Sep. 2
H2O
Unreacted
H2S, CO2
CO, H2, SO2
Sep. 3
SO2
Unreacted
H2S, CO2
CO, H2
Sep. 4
Unreacted H2S, CO2