



# Apparatus and process for energy self-sustainable and high-yield conversion of acid gases (H<sub>2</sub>S and CO<sub>2</sub>) into syngas

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## ARTICLE INFO

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Regenerative thermal reactor

## ABSTRACT

H<sub>2</sub>S and CO<sub>2</sub> are two well-known emissions with cumbersome management and not yet established bulk utilization plans. The invention converts H<sub>2</sub>S and CO<sub>2</sub> in syngas and, as the only by-products, elemental sulphur and water by means of a dedicated (i) Regenerative Thermal Reactor (RTR) and (ii) Acid Gas to syngas (AG2S) process layout thanks to the overall reaction:  $2\text{H}_2\text{S} + \text{CO}_2 = \text{H}_2 + \text{CO} + \text{S}_2 + \text{H}_2\text{O}$ . The reaction is globally endothermic, but it can energetically supplied in situ thanks to a minor injection of oxygen/air. The oxygen injection generates the exothermic reaction  $\text{S} + \text{O}_2 = \text{SO}_2$  in an appropriate amount so as to achieve and preserve the optimal conversion temperature. The SO<sub>2</sub> generated for energy sustainability is therefore converted within the process layout. The once-through conversion is 75%v for the H<sub>2</sub>S and 50%v for the CO<sub>2</sub>. The unreacted reactants are split from the syngas and by-products and recycled upstream for complete conversion. The invention is the first process utilizing no sources, neither bio nor fossil, but only emissions to generate syngas and, hence, hydrogen. Two moles of syngas are obtained every three moles of emissions, also achieving the total neutralization of H<sub>2</sub>S and a relevant cut of CO<sub>2</sub>. Technology development has reached out the industrialization level. The laboratory testing has been developed in Politecnico di Milano, at the facilities of the Center for Sustainable Process Engineering Research (SuPER); the bench-scale tests have been exerted at the Sotacarbo Sustainable Energy Center SpA facilities and the industrial application is just started at Itelyum Regeneration srl, an ecorefinery for exhausted oil recovery.

### Value of the invention

- The invention is useful to mitigate the grand challenges of our century by means of the bulk utilization of CO<sub>2</sub> emissions and without any resource exploitation. When co-present, CO<sub>2</sub> is directly captured together with H<sub>2</sub>S by means of traditional sweetening processes and provided to the AG2S (Acid Gas to syngas) process.
- All the processes for syngas production and treating fossil and bio-sources containing sulphur can benefit from the invention to cut the CO<sub>2</sub> emissions. The sulphur content is removed and transformed in H<sub>2</sub>S, which is therefore coupled with CO<sub>2</sub> to produce additional syngas. The syngas is therefore converted in chemicals (methanol, dimethyl ether, acetic acid) or other products.
- The invention receives the tail gases of oil- or bio-refineries, gasification plants, shale-oil and gas fields, geothermal wells, rubber chemical recycling to quote a few and it is applied in non-invasive way to buster the production of final products without any further

exploitation of resources, but simply reconvert back the emissions in additional product.

- The invention consists of a Regenerative Thermal Reactor (RTR) able to convert the 50%v of CO<sub>2</sub> and the 75%v of H<sub>2</sub>S in the once-through step. Such a reactor is integrated in a new process layout (Acid Gas to syngas (AG2S) process) that guarantees 100% selectivity and 90% yield to syngas with optimal feedstock and optimal operating conditions.

### 1. Invention description

This invention, already validated in laboratory and in a pilot plant, is industrially applicable in the oil & gas field and to sulphur recovery units (SRU) of existing plants and is based on a well-established technology for other uses different from H<sub>2</sub> production, starting from sulphur and steam; so, the risk of failure is minimized.

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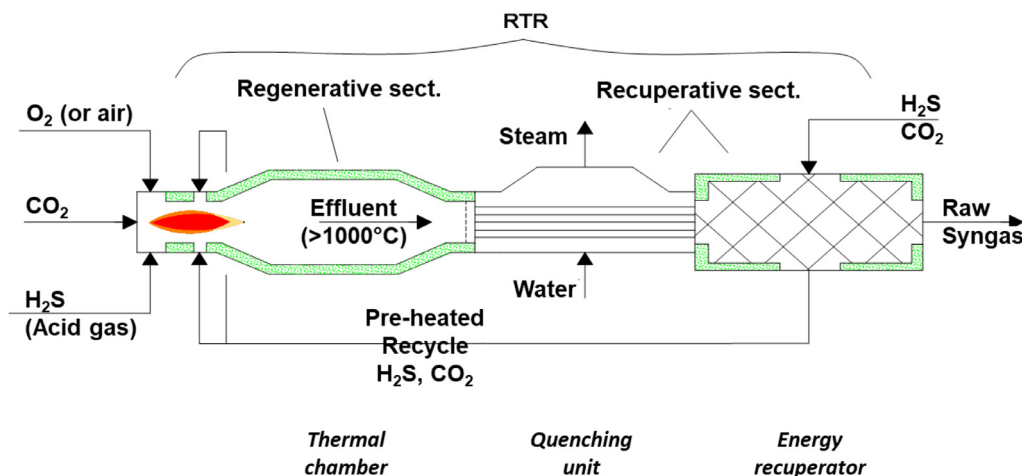


Fig. 1. Regenerative thermal reactor (RTR) configuration.

Moreover, this new technology does not require heavy modifications to existing plants having a Claus unit (the investment required for refurbishing is rather small in comparison to the building of a new technology plant). The refurbishing is worthy in all scenarios with payback periods ranging from 0.5 years (best scenario) to 1.7 years (worst scenario).

The geographic distribution of the target market is worldwide.

## 2. Application potential

The kernel of the invention is based on the Regenerative Thermal Reactor (RTR) (Fig. 1). It consists of three elements:

### 2.1. A thermal chamber

It is an in-line refractory chamber that rises the temperature of the system thanks to a minor injection of oxygen/air, which oxidizes part of the  $H_2S$  and where the overall oxyreduction reaction:



takes place. A bunch of side reactions takes also place providing other by-products than elemental sulphur and water [1], but all these compounds are appropriately handled and converted back to reactants in the AG2S process. The main compounds are reported in Fig. 2. Fig. 2 reports experimentally validated trends obtained using DSmoke suite, a property package for kinetic-based simulation [2], for non-optimal feedstock and non-optimal operating conditions (temperature of the thermal chamber = 1300 °C) for the once-through conversion in the thermal chamber of RTR. Table 1 illustrates two extreme conditions of the operational domain ( $T = 1000$  °C and  $T = 1500$  °C).

$CO_2$  and  $H_2S$  conversions are in line with the general yield of the technology: 25.6–55.3%v and 34.0–85.6%v, respectively. Syngas and by-product productions are balanced at low temperature. Higher temperatures require more oxygen injection and, therefore, more oxidation leading to higher yields but also higher production of by-products.  $SO_2$  is also increasing with the temperature, but its concentration remains significantly lower than the one of the Claus processes. At last, some organosulfur compounds, here represented by COS, are formed, but they will be removed in situ thanks to the AG2S process configuration.

### 2.2. A quenching element

The radical compounds generated in the thermal chamber are very sensitive to recombination back to the reactants [3]. The recombination effects can significantly impact the once-through conversion of the RTR and, hence, the volume of all the units and recycle streams constituting

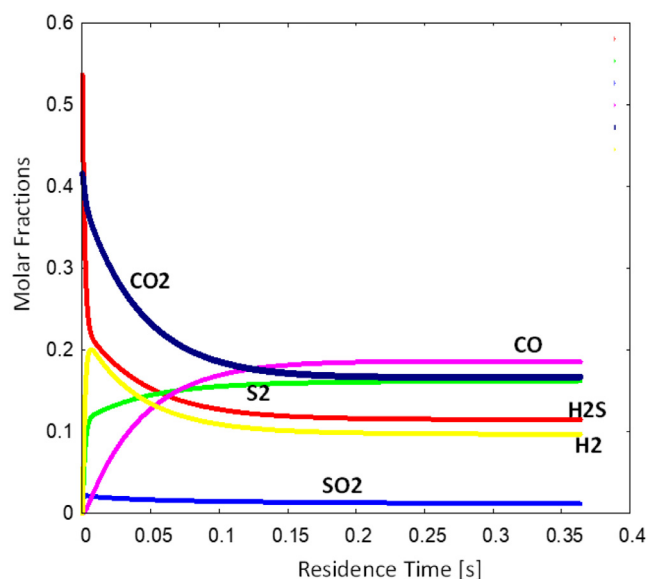


Fig. 2. Molar composition along the axis of the thermal chamber of RTR using non-optimal feedstock and non-optimal conditions. The once-through yield for  $CO_2$  and  $H_2S$  is confirmed. The syngas has a quality  $H_2/CO$  ratio close to 0.6. The presence of  $SO_2$  is due to the minor injection of oxygen for energy self-sustainability. The only missing relevant compound is water, which can be evaluated by difference with the thermal chamber effluent.

Table 1

Effluent of the thermal chamber of RTR at the feasible operational boundaries ( $1000$  °C <  $T$  <  $1500$  °C).

INLET			
Temperature	°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
OUTLET			
Thermal chamber T	°C	1500	1000
$CO_2$	kmol	4.47	7.44
$H_2S$	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
$H_2O$	kmol	19.16	6.16
COS	kmol	0.13	0.33

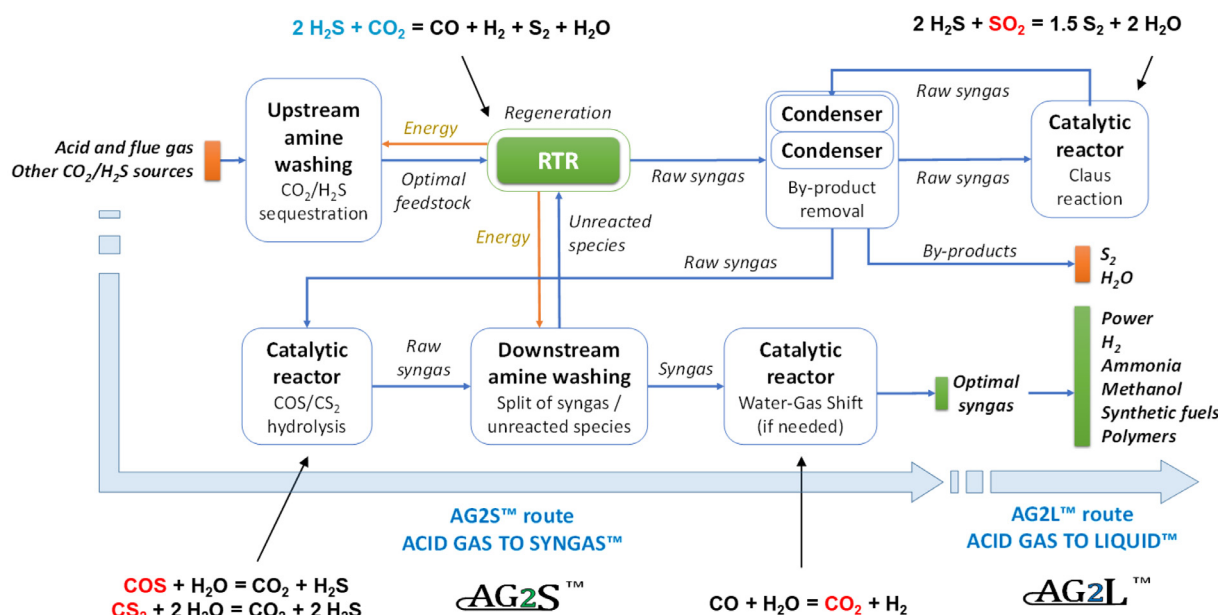


Fig. 3. AG2S process layout.

the AG2S process. To prevent recombination effects, it is necessary to fast cold down the temperature of the thermal chamber effluents. Temperature drop is easily achieved by means of a boiler with boiling feed water and medium pressure steam generation. The recombination effect is active until the molecule of H<sub>2</sub>S is thermally decomposed. This condition occurs for temperatures higher than 880 °C. The quencher is therefore useful to drop the temperature of the effluent down to about 850 °C.

### 2.3. An energy recuperator

A gas/gas feed/effluent heat exchanger is adopted to refine the temperature of the effluent of the RTR. From the outlet temperature of 850 °C achieved in the quenching element, the energy recuperator must decrease the temperature to about 300 °C by exchanging with the fresh acid gases coming in counter-current from the sweetening processes. Special materials are required for this part of the RTR.

The acid gases come from the upstream sweetening processes and enter from the right side of RTR of Fig. 1 in the shell side of the energy recuperator. They are preheated by the hot raw syngas outflowing the RTR in the tube side. In the start-up phase, this energy recovery is not yet possible, and a major injection of oxygen/air is required. Once preheated, the acid gases enter the thermal chamber, possibly corrected in their temperature by a by-pass of cold acid gas stream. There, they encounter the injection of oxygen/air which oxidizes a relatively small portion of H<sub>2</sub>S according to the overall reaction:



The exothermicity of such reaction rises the temperature of the thermal chamber up to the desired temperature according to the amount of oxygen supplied. The overall reaction (1) takes place in the thermal chamber at a temperature in the range of 1000 - 1500 °C according to the desired conversion and final quality of syngas. The effluent of thermal chamber is said *raw syngas* due to the presence of non-reacted reactants and other by-products. The hot raw syngas exits the thermal chamber and enters the quenching element, tube side, while boiling feed water is provided at the shell side. The boiling feed water vaporizes by cooling down the gas stream to about 850 °C. The steam production is generally at medium pressure, but it is related to the energy integration of the pro-

cess with the rest of the plant and utilities. The final cooling is given to the raw syngas by the energy recuperator: the temperature drops down to about 300 °C.

The overall reaction (1) is accompanied by other side reactions generating organosulfur compounds such as COS and CS<sub>2</sub>. It is therefore mandatory to insert the RTR in the dedicated process layout reported in Fig.3. An upstream sweetening process is adopted to capture acid gases. It could be either an amine washing or whatever other technology that achieves the target. It is usually already present by the field. The CO<sub>2</sub> concentration is usually higher than the H<sub>2</sub>S concentration in the acid gas streams, contrarily to what is required by reaction (1). The sequestration step must foresee a ratio correction to partially remove the surplus of CO<sub>2</sub>, if any. The practical H<sub>2</sub>S/CO<sub>2</sub> ratio to be considered strongly depends on the thermal chamber temperature, but it is in the range of 2.2–4.0; lower yields are obtained, otherwise. In the RTR, acid gases are partially converted into syngas, but also in elemental sulphur and water as reaction (1) by-products; moreover, SO<sub>2</sub> is generated due to the energy sustainability and organosulfur compounds are also formed due to side reaction mechanisms. This stream is called the *raw syngas*. A first purification step is represented by the sulphur and water condensers, which physically remove the main by-products in two steps. Then, thanks to the presence of a relevant amount of unreacted H<sub>2</sub>S, the SO<sub>2</sub> is totally converted in a traditional Claus converter by means of the catalytic reaction:



which takes place on a gamma-alumina bed at 300 °C. The relevant composition of H<sub>2</sub>S with respect to SO<sub>2</sub> ensures the total conversion of this latter compound. The additional elemental sulphur and (partially) water are condensed and separated. The raw syngas is now cleaned by elemental sulphur, water and SO<sub>2</sub>. Only a few of ppm of sulphur are still present in the vapors and a hydrogenation step could be inserted to completely clean the stream. The organosulfur compounds and unreacted reactants are still spoiling the syngas stream. Using commercial catalyst, COS and CS<sub>2</sub> are totally hydrolysed:



The water remaining acts as reactant for hydrolysis reactions. The relevant aspect is that the hydrolysis step completely neutralizes the organosulfur compounds giving back the reactants. In such a way, the 100% selectivity of the process is ensured. At last, a smaller, but additional, sweetening step is necessary to split the good syngas from the remaining H<sub>2</sub>S and CO<sub>2</sub>, which are not reacted in (1), but also coming from the hydrolysis of organosulfur species. The acid gases recovered by this step are recycled back to the RTR, whereas the good syngas is sent downstream. According to the uses of the produced syngas, a water-gas shift reactor could be included in the process layout to optimize the H<sub>2</sub>/CO ratio to favor downstream conversions. The methanol synthesis, for instance, requires H<sub>2</sub>/CO ratio of 2.1 on commercial CZA catalyst [4].

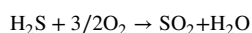
### 3. Background

In the USPTO Office Action, the examiner did not cite any relevant (for the patentability requirements) prior art document but only required formal changes in the text to overcome clarity objections.

During the prosecution of the EP patent application, the examiner cited five prior art documents.

The process described in the closest prior art [5] made use of an electrically heated surface for producing syngas starting from CO<sub>2</sub> and H<sub>2</sub>S.

In the invention, the energetic supply is provided by the following exothermal reaction:



Therefore, starting from the prior art document, the technical effect obtained with the process of the invention is a considerable energy-saving.

The objective technical problem solved with this invention may be seen as to provide an alternative process for producing synthesis gas, comprising the endothermic reaction between CO<sub>2</sub> and H<sub>2</sub>S.

Another piece of prior art [6], cited in the search report, claimed a similar process for the oxidation of H<sub>2</sub>S to SO<sub>2</sub> but carried out in different operating conditions (lower temperatures and by using a catalyst – V<sub>2</sub>O<sub>5</sub> or V<sub>2</sub>S<sub>5</sub>). These differences made sure to overcome the inventive step objections.

The same arguments may be applied to another cited document [7], claiming a process for the oxidation of H<sub>2</sub>S to elemental sulphur and/or SO<sub>2</sub>, using a catalytic system.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

### CRediT authorship contribution statement

**Massimo Barbieri:** Data curation, Writing – review & editing. **Flavio Manenti:** Conceptualization, Investigation, Data curation, Writing – original draft.

### Acknowledgments

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### Specifications table

<b>Subject code</b>	1500 General Chemical Engineering
<b>Specific subject area</b>	The invention can be classified as an industrial process that improves the production of syngas, reducing H <sub>2</sub> S and CO <sub>2</sub> emissions.
<b>Industry code</b>	C01B17/04 (EP,US): Sulphur; compounds thereof • Preparation of sulphur •• Purification - from gaseous sulphur compounds including gaseous sulphides.
<b>Details of inventors</b>	Flavio Manenti (flavio.manenti@polimi.it; Politecnico di Milano) Lucio Molinari (consultant) Sauro Pierucci (sauro.pierucci@polimi.it; Politecnico di Milano), now retired
<b>Dates of invention</b>	The invention was conceived in 2012 (proof of concept) and publicly disclosed in 2014 (after the filing of the priority patent application).
<b>Patent details</b> <i>(Only if patented)</i>	The priority patent application was filed in 2013 with the number ITMI20131322A1 Date patent granted: July 5th, 2016 Patent owner: Politecnico di Milano Patent attorney or agent: Raffaella Consuelo Asensio (Perani & Partners) Contact for service: Massimo Barbieri Link to patent: <a href="https://www.uibm.gov.it/bancadati/Advanced_search/type_url?type=pt&amp;cl=1">https://www.uibm.gov.it/bancadati/Advanced_search/type_url?type=pt&amp;cl=1</a> The Italian patent application was extended with the PCT procedure in 2014. The national/regional entries were carried out in 2016 in the following countries: EPO, EAPO, USA, Canada and China. The European patent application was granted in 2019, with the number EP3027552B1 and validated in: Italy, France, Germany, United Kingdom, Spain, Denmark and Nederland. No opposition was filed within nine months from the date of grant. Link to the patent: ( <a href="https://worldwide.espacenet.com/patent/search?q=pn%3DEP3027552B1">https://worldwide.espacenet.com/patent/search?q=pn%3DEP3027552B1</a> ) The Eurasian patent application was granted in 2018, with the number 031340B1. Link to patent: <a href="https://www.eapo.org/en/patents/reestr/patent.php?id=31340">https://www.eapo.org/en/patents/reestr/patent.php?id=31340</a> The Chinese patent application was granted in 2018 with the number CN105531222B. Link to patent: <a href="https://worldwide.espacenet.com/patent/search?q=pn%3DCN105531222B">https://worldwide.espacenet.com/patent/search?q=pn%3DCN105531222B</a> The US patent application was granted in 2017 with the number US 9,630,839 B2. Link to patent: <a href="https://worldwide.espacenet.com/patent/search?q=pn%3DUS9630839B2">https://worldwide.espacenet.com/patent/search?q=pn%3DUS9630839B2</a> The Canadian patent application has been granted in 2021 Link to the application: <a href="https://www.ic.gc.ca/opic-cipo/cpd/eng/patent/2918458/summary.html?query=%28manenti%29&amp;start=&amp;num=&amp;type=advanced_search">https://www.ic.gc.ca/opic-cipo/cpd/eng/patent/2918458/summary.html?query=%28manenti%29&amp;start=&amp;num=&amp;type=advanced_search</a> All patent family members are in force.
<b>Intended use</b>	This invention is available for licensing or selling to a company interested in developing an industrial plant.
<b>Funding / sponsor acknowledgments</b>	This invention did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

(continued on next page)

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**Related research article**

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**Related other sources:**  
(datasets, software,  
diagrams, plans, etc.)

None.

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