



Mitigating Carbon Dioxide Impact of Fossil/Bio-refineries by Acid Gas to Syngas Technology: Sensitivity Analysis and Techno-economic Assessment

Anna Dell'Angelo¹, Ecem M. Andoglu², Giulia Bozzano¹, Suleyman Kaytakoglu³, Flavio Manenti^{*1}

¹CMIC Dept. "Giulio Natta", Polytechnic University of Milan, 32 Piazza Leonardo da Vinci, Milan, 20133, Italy

e-mail: anna.dellangelo@polimi.it, e-mail: flavio.manenti@polimi.it, e-mail: giulia.bozzano@polimi.it

² Chemical Engineering Department, Bilecik Seyh Edebali University, Gulumbe Campus, Bilecik, 11230 Turkey

e-mail: muge.andoglu@bilecik.edu.tr

³ Department of Chemical Engineering, Eskisehir Technical University, Iki Eylul Campus, Tepebasi, Eskisehir, 26555, Turkey

e-mail: skaytako@eskischir.edu.tr

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ABSTRACT

Hydrogen sulfide is a highly toxic by-product in the refineries. Traditional sulfur recovery units are already used, but optimization studies on them are still limited. The proposed process evaluates the possibility of a new frontier for sulfur recovery and carbon dioxide emissions reduction in refineries. The technological kernel is the regenerative thermal reactor which allows to convert hydrogen sulfide with another challenging emission, carbon dioxide, to valuable products (syngas) and harmless compound as elemental sulfur and water. The work has compared the effectiveness of the proposed technology with the traditional sulphur recovery units in terms of techno-economics and environmental impacts by proposing several sensitivity analyses on the main process parameters. Results state that it greatly improves the sustainability of the process in terms of quality of syngas produced while limiting the emissions. The economic analysis results look to be very promising for a pilot plant setup.

KEYWORDS

Carbon dioxide utilization, Low emissions, Syngas, Claus process, Hydrogen sulfide, AG2STM.

INTRODUCTION

Oil refineries and gasification of coal, biomass, and organic waste [1] are, in the last years, major producers of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) emissions with related greenhouse effect, that lead to environmental concerns [2]. The stringent H₂S environmental thresholds have triggered renewed interest in the modelling of sulfur chemistry [3]. Hydrogen sulfide is a very common and toxic by-product in fossil/bio-refineries, gas fields, geothermal and petrochemical processes, in fact, it is a well-known poison for industrial catalysts and its combustion products are responsible for acid rains. Nonetheless, H₂S is a molecule very rich in hydrogen content, the richest one after methane, hydrocarbons, and ammonia.

Assuming this, H₂S is not only a contaminant that as to be oxidized and converted into not harmful products (i.e. Claus process), but a new hydrogen source to be tapped in order to

* Corresponding author

produce more modern and appealing products to self-sustain from economic and environmental viewpoint the whole process.

Carbon dioxide is responsible for a great impact on the environmental system [4] without relevant industrial uses due to its thermodynamic stability and low chemical value. The environmental concerns relating to CO₂ as a greenhouse gas pushed toward a challenging carbon dioxide sequestration by different processes: chemical-physical washing and consequential disposal in remote storage [5]. Nowadays, the carbon capture and storage (CCS) technology has been studied by various researchers [6]. The process covers a broad range of technologies that are being developed to allow carbon dioxide emissions from fossil fuel using at large point sources in order to be transported to safe geological storage, rather than being emitted to the atmosphere [7].

In the last decade, scientific and technical efforts were made to mitigate the CO₂ impact and other contaminants (i.e. hydrogen sulfide) by reducing its net production with renewable energies. Despite this, nowadays CO₂ is used as a feedstock in only two large-scale industrial processes, such as methanol-and urea [8] synthesis that are able to mitigate only 1% of carbon dioxide emissions, despite the high capacity of those plants. Some promising processes, for recycling CO₂, are also Fisher-Tropsch synthesis [9] and catalytic CO₂ but they still are in a demonstrative scale or they are high energy-consuming [10].

The sulfur removal technologies are found, instead, in very different stages of innovation, some are deeply studied as the thermal decomposition [11]; others are found in the pilot stage or at the threshold of demonstration [12][13]. Some others are in a very early stage of technical development or in the conceptualization stage for example [14] have studied a non-thermal plasma reaction, in which the cold plasma conditions and the adoption of dedicated catalysts can achieve high H₂S conversion but the residence time appears significantly long.

Most of the recent studies are focused on carbon dioxide capture and sulfur recovery individually, so acid gas treatment researches are still limited. *Kalatjari et al.* [15] has set a dynamic pilot plant to carry out CO₂ capture from acid gas using the aqueous mono-ethanolamine (MEA) at various concentrations and temperatures and considered different thermodynamic models to calculate absorption and desorption of carbon dioxide in gas feed varying CO₂ concentration in acid gas feed. *Ibrahim et al.* [16] proposed a modification for Claus process in order to increase sulfur recovery efficiency from acid gas, reduced the number of catalytic unit and hence, lowered the operating cost. Along with these new technologies, numerical and experimental examinations are still an interesting research topic. *Groisil et al.* [17] have studied on acid gas removal for syngas, using a modified mechanism to simulate the pyrolysis of acid gas, with due accounting for pyrolysis and oxidation reactions. In 2016, a laboratory-scale reactor for producing syngas from acid gas had been used by [18] to provide information on different operating conditions.

Acid gases often contain other impurities that include nitrogen (N₂), ammonia (NH₃), carbon disulfide (CS₂), carbonyl sulfide (COS), and hydrocarbons such as benzene (C₆H₆), toluene (C₇H₈), and xylene (C₈H₁₀) (BTX). At industrial level the standard Claus process is commonly used for the treatment of acid gas to recover elemental sulfur [19]. However, the efficiency of this process is significantly hindered by the presence of impurities and compositional variations of acid gas in the feed stream to Claus plant; in particular, the high content of CO₂ in acid gases poses several environmental and technical issues in the operation of Claus plants [21].

The proposed technology (AG2S™ – Acid Gas to Syngas) exploits the amount of CO₂ without any use of hydrogen or costly reducing agents; in fact, another emission, H₂S, CO₂ without any use of hydrogen or costly reducing agents; in fact, another emission, H₂S, is coupling with it for producing syngas and consequently other valuable chemicals (ammonia and liquid fuels) [22][23]. According to the overall reaction:



The reaction is possible when both the molecules are in co-presence, so this technology allows to use energy sources currently unexploited such as crude oils, natural gases, geothermal sources, and different coals [24]. It is important to point out that such a reaction is chemically nobler than the traditional Claus reaction, as the hydrogen in H_2S is not nailed in water, but it is freed to form hydrogen. This is an attractive alternative, also because the large volume of CO_2 in lean acid gas can be captured from the produced syngas and recycled back to produce other syngas.

The presence of impurities, such as hydrocarbons in acid gas will also be an added value since this will favour a higher yield of syngas. Moreover, hydrogen (H_2) and carbon monoxide (CO) produced, can then, be used in industry for energy and power generation, in fact, syngas is a valuable commodity fuel in gas engines too. All these considerations have pushed research and development for captive use of H_2S and CO_2 to improve the accounting of these by-products [25].

The aim of this work is to demonstrate the sustainability and feasibility of the technology, applied to real industrial cases and comparing it with the Claus process considering some critical parameters (H_2S and CO_2 conversion, reaction temperature, recombination effects and carbon dioxide reuse). To test its potential at industrial level, a techno-economic estimation involves both the CAPEX and OPEX aspects was carried out to take in account an industrial data of SRU plants and building a greenfield case for the new technology. Exploiting extensive scientific works and experimental and operating experience, the new route process looks to be very promising.

PROCESS DESCRIPTION AND MODELLING

In this section, process descriptions, initial conditions and computational tools were given. DSMOKE[®] software was used for simulating Claus process and AG2S[™] technology.

Operating conditions

In the furnace, the temperature range is between 1223 and 1573 K and the pressure varies from 1.01 to 1.51 bar, along with the waste heat boiler is simulated at 640 K. It is well known that acid gases contain a considerable amount of CO_2 . In order to estimate the reuse of CO_2 , the models were also run with different percentages of CO_2 inlet compositions varying from 25% to 44% at 1373 K and 640 K in the thermal furnace and WHB respectively. The innovative reaction can be used when streams with both CO_2 and H_2S are presented. Temperature and pressure ranges were chosen according to the average operation temperatures reported in the literature.

Claus process

In a typical Claus process, the thermal part consists of a burner, a thermal furnace (TR) and a waste heat boiler (WHB). In this study, the burner and thermal furnace were modelled as one plug flow reactor, and the waste heat boiler was simulated as a bundle of several PFRs as shown in **Figure 1**.

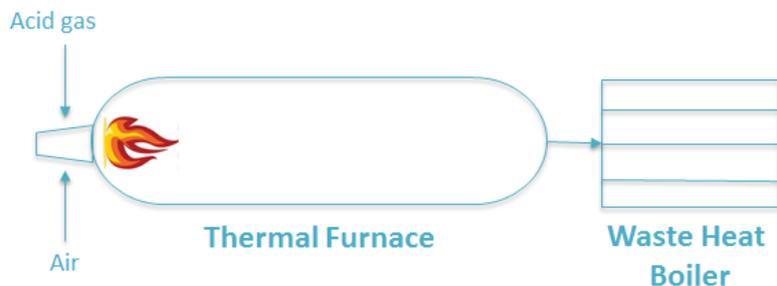


Figure 1. Thermal section of a typical Claus process

The horizontal furnace reactor was modelled by assuming:

- Steady-state operation condition;
- Adiabatic condition (well-isolated furnace);
- Ideal gas mixture (due to high temperature and low pressure);
- Fully developed flow both in TR and WHB;
- Absence of fouling;
- Inlet streams are acid gas and air. Air can be enriched by oxygen supply.

In this work, the air was not enriched and was carried with 21% of oxygen. **Table 1** shows the properties of inlet streams of sulfur recovery unit (SRU) obtained from industrial plants and used also for simulating the novel technology, suitably separating the main flow from the impurities.

Table 1. Inlet operating conditions and geometry parameter

	Acid gas	Air
Flowrate (kg/h)	4230	8907
Temperature (K)	398	318
Pressure (bar)	1.59	1.59
Composition (% molar)		
H ₂ S	0.7955	0.000
CH ₄	0.021	0.000
N ₂	0.000	0.714
O ₂	0.000	0.189
C ₂ H ₆	0.014	0.000
C ₃ H ₈	0.019	0.000
H ₂ O	0.064	0.097
CO	0.003	0.000
CO ₂	0.066	0.000
H ₂	0.004	0.000
NH ₃	0.005	0.000
TR length (m)	6.500	
TR internal Ø (m)	1.550	
WHB length (m)	6.000	
WHB internal Ø (m)	0.050	
WHB tube number (-)	470	

The oxidation reactions take place in the flame zone that is 0.1 - 0.5 m of the furnace. The other reactions occur along the thermal section of the reactor.

At high operating temperatures, S_2 is the dominant allotrope of the elemental sulfur. Therefore, in this work, elemental sulfur was mentioned as S_2 , even if, it has allotropes such as S_1 to S_8 .

Acid Gas to Syngas technology

The thermal section of AG2STM process is made by regenerative thermal reactor (RTR), which has a different configuration compared with Claus process. It has a thermal reactor, waste heat boiler and a heat exchanger. The main point is to feed the preheated acid gas with an optimal H_2S/CO_2 ratio. Therefore, the demanding oxygen or air stream is much lower than the one required in Claus process. Thermal reactor and WHB were simulated considering them as an adiabatic and a non-isothermal PFRs, respectively.

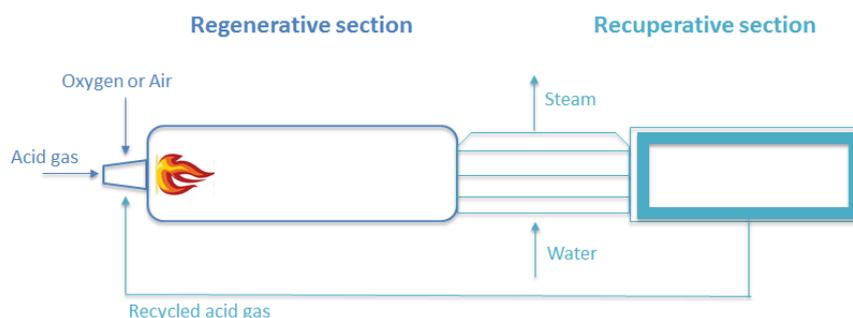


Figure 2. AG2STM process scheme

Computational environment

AG2STM process was studied using the Simulation Suite PRO/II® by Schneider-Electric Simulation Science, using SRK (Soave-Redlich-Kwong) equation of state as thermodynamic model. The process scheme of the AG2STM is shown in Figure 2. In order to use this technology at industrial level, it is necessary to revamp existing Claus plants, modifying some of the current used unit operations, in particular the thermal furnace and keeping unchanged the catalytic section. The design of the new reactor has allowed the overcoming of the problem: the implemented solution consists in a thermal regenerative reactor (RTR). In this configuration the efficiency of the process is improving by burning a proper amount of H_2S in order to minimize generation of steam and obtained an autothermal reactor.

Fresh reactants (CO_2 and H_2S coming from upstream plants, assisted by air or oxygen) are injected along with recycled reactants into RTR. The recycle can be also mixed with fresh reactants before pre-heating and injection into the reactor recycle for improving self-sustainability of the plant from process standpoint, that is, for reduction or elimination of exhausts.

For assuring a proper production yield, it is essential to prevent any possible recombination effects, which have been proven to be significant during relatively slow cooling; for this purpose, a Waste Heat Boiler (WHB) is installed just at outlet of RTR to quench the reactions.

The WHB and recycle pre-heating equipment play a key role in the regenerative process, therefore, they could be considered a portion of the RTR. On the whole, the RTR could be also seen as a system constituted of a “regenerative” and a “recuperative” section, and not just the reaction chamber itself.

As mentioned the aim of this process is to recover as much as possible hydrogen from the H_2S molecule, in order to be able to produce a huge amount of syngas. In order to allow the pyrolysis of H_2S high temperatures (1273 - 1473 K) [26] are necessary to: (i) activate the reactive system from chemical-thermodynamics standpoint, (ii) quicken kinetics and (iii) reduce by-products.

The outflow of the catalytic reactor, which includes a certain amount of syngas, must be purified from the unreacted acid gas (H_2S and CO_2). The simulation of the catalytic reactor is carried out using conversion reactor in Pro/II. Al_2O_3 sites hydrolyse COS and CS_2 and support the

dispersed elements that allows to increase the conversion up to 70% in the new technology and it is about 99% for Claus reaction [27].

The AG2STM technology approach at real plant results to be a novelty, both processes were simulated with several field data using DSMOKE. The software is a general framework developed by our research group for numerical simulations of reacting systems with detailed kinetic mechanisms including thousands of chemical species and reactions [19], involving radicals and complex mechanism to explain all the main reactions of the process.

For each reactor, 146 species mass balances, one global mass balance and one energy balance were solved, using standard material (eq. (2)) and energy balances (eq. (3)) of plug flow reactor:

$$\frac{dw_i}{dt} = \sum_{j=1}^{NR} \varphi_{i,j} R_j W_j \quad i = 1, \dots, NC \quad (2)$$

$$c_p \frac{dT}{dt} = \sum_{j=1}^{NR} -\Delta H_j R_j + \frac{U_{\text{ext}} S}{V} (T_{\text{ext}} - T) \quad (3)$$

RESULTS AND DISCUSSION

In this section, simulation, recombination effects, carbon dioxide effect of refineries and Greenfield economic assessment results were given.

Simulation results

The evaluation of the potential application of AG2STM technology on sulfur recovery is related to the quantity of H₂S presents in the feedstock. In this work to prove the validity of the process a feedstock containing 23% of H₂S was chosen. The feed composition is reported in **Table 1**. Because Claus process operates at quite high temperatures, the temperature range was chosen as 1223 - 1573 K in this work.

According to the simulation results, **Figure 3** shows the dependence of H₂S conversion, of both processes, in function of the temperature. The conversion of H₂S is increasing gradually with an increase of temperature and achieving 70% and 83% for AG2STM and Claus processes, respectively.

The acid gas and air meet in the burner, which is the first step of the Claus furnace. In that part, hydrogen sulfide conversion increases fast depends on the oxidation reactions, in fact the conversion at all temperatures are in a range of 70 - 83%.

Instead, in AG2STM technology the feed is preheated in order to achieve the maximum hydrogen sulfide conversion. The reaction between H₂S and CO₂ (Equation 4) occurs immediately due to high activation energy. The hydrogen sulfide conversion achieve minimum $\approx 30\%$ at 1223 K and maximum $\approx 70\%$ at 1573 K. These results show that the conversion is strongly dependent of operating temperature.

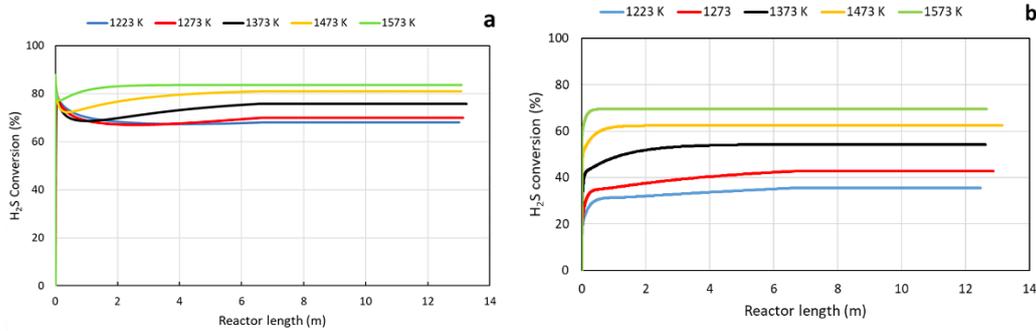


Figure 3. Conversion of H₂S in Claus (a) and AG2STM (b) in function of temperature (K)

Together with decreasing H₂S content, one of the main purposes of AG2STM process is to quantify the production of syngas. It is a valuable commodity for use as a fuel in gas engines or to produce valuable chemicals such as ammonia and liquid fuels.

Yield of syngas is an important indicator of process feasibility. It is defined as ratio between moles of syngas and moles of reagents:

$$\eta_{\text{syngas}} = \frac{F}{F^0} \frac{x_{\text{CO}} + x_{\text{H}_2}}{x_{\text{CO}_2}^0 + x_{\text{H}_2\text{S}}^0}, \quad (4)$$

where x_i is the molar fraction, F is the molar flow rate and F^0 the initial conditions.

The yield of syngas producing respect to initial reagents is shown in Figure 4. Hydrogen and syngas production have been widely studied. According to [28], the temperature is the most influent factor for pyrolysis, and increasing the temperature, resulted in increase in gas yield and more hydrogen production. The optimization of temperature is around 1473 K for the process. The results illustrated that higher temperature was needed in the process up than 1373 K to maximize syngas yield.

The low temperatures are not able to activate the reactive system from chemical-thermodynamics standpoint; hence, at the temperatures lower than 1373 K, the syngas yield is very low and the time which is needed for the occurrence of main reactions is longer. Besides, the side reactions completely occur along with the main reactions at 2.5 m, 0.4 m, and 0.25 m at the temperatures 1373 K, 1473 K, and 1573 K, respectively. The peaks show that the reactions take place quicker and the yield rises by increasing the temperature, as expected.

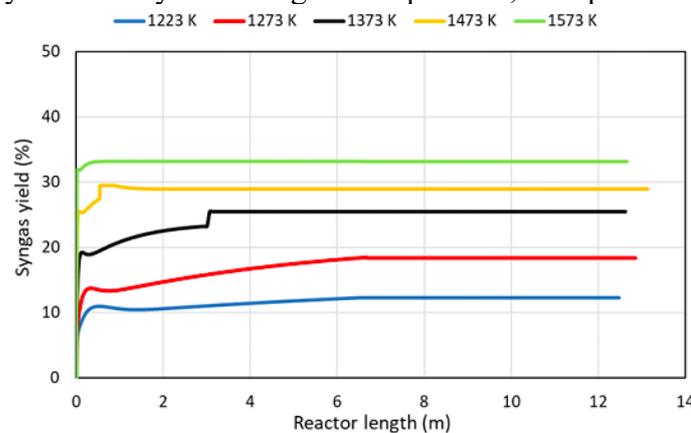


Figure 4. Syngas yield AG2STM technology in function of operating temperature (K) and reactor length

Table 2 shows the molar fraction of CO₂ in function of operating temperature. As seen in table CO₂ conversions, obtained from Claus furnace are almost equal at any considered temperature. Instead, the new technology is strongly dependent on the temperature and achieves the best CO₂ conversion up than 1473 K.

Table 2. CO₂ molar fraction in thermal reactor and waste heat boiler outlets

<i>Temperature (K)</i>	AG₂STM technology		Claus process	
	<i>TR outlet</i>	<i>WHB outlet</i>	<i>TR outlet</i>	<i>WHB outlet</i>
1223	0.1706	0.1709	0.0409	0.0425
1273	0.1358	0.1368	0.0426	0.0439
1373	0.0914	0.0915	0.0447	0.0455
1473	0.0741	0.0743	0.0397	0.0402
1573	0.0607	0.0611	0.0329	0.0336

Recombination effects

The hydrogen sulfide decomposition reaction plays an important role in the formation of CO and COS. In fact, the recombination reactions (eqs. (5)-(7)) that occur at the front of the WHB are:



These reactions not only influence sulfur recovery, air demand, and hydrogen production in the SRU, but they also affect the performance of the WHB.

The COS and CS₂ are formed in the front-end units, i.e. the TR and the WHB. They can be converted to H₂S and CO via hydrolysis reactions in the catalytic converters. The main reaction occurring in the converters is favoured thermodynamically at lower temperatures (623 K). At these temperatures the hydrolysis reactions are kinetically limited which often results in little conversions of COS and CS₂. The unconverted COS/CS₂ end up in the tail gas where they represent a large proportion of the sulfur content. The temperature profile's trend shows a great stability of the COS species at high temperature (1273 - 1573 K) while it is possible to note an inverse trend for the CS₂ species which is more stable at low temperature. The formation of these species is mainly due to the presence, albeit in small quantities, of H₂S in the WHB unit in which the reactions eq. (6) and eq. (7) take place.

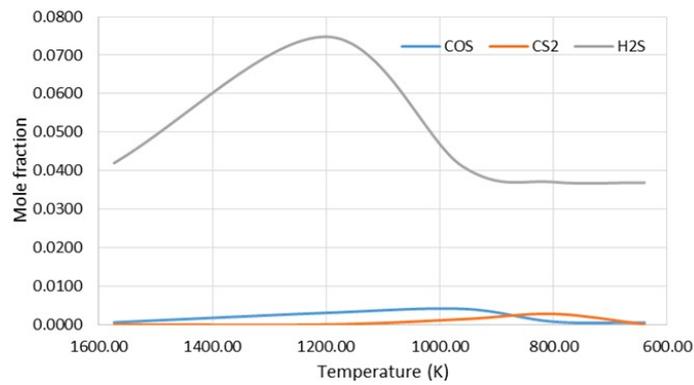


Figure 5. Recombination products concentrations of WHB in function of temperature

Investigation of carbon dioxide effect of refineries

The investigation of CO₂ effect was done by taking into account three feed based on different CO₂ content, because it is well-known that AG2STM achieves its better performance with high CO₂ content. The data of two Oil Refinery Companies located in Mesaieed, Qatar and one in Nanjing, China are used as references. They were mentioned in this study as case study 1, 2 and 3 which contain 25 mol %, 39 mol % and 44 mol % of carbon dioxide respectively.

As seen in **Figure 6**, CO₂ effect are strongly influence of feed composition, this shows that efficiency of AG2STM process is strongly dependent on inlet CO₂.

The results illustrate that the novel technology has a significant predominance comparing with Claus process in terms of CO₂ conversion. Following the graph in **Figure 6** (straight line), there is a linear dependence between the CO₂ content and its conversion, in fact the process achieves 27% conversion when the molar composition is 44%. In the Claus process in **Figure 6** (dotted line) the trend is the reverse and the conversion is low (1.5 - 6%), due to a not optimal figuration; in fact, reducing CO₂ is not the main target of this process. However, the reactions occur in the furnace are not able to eliminate carbon dioxide sufficiently, a further step is required.

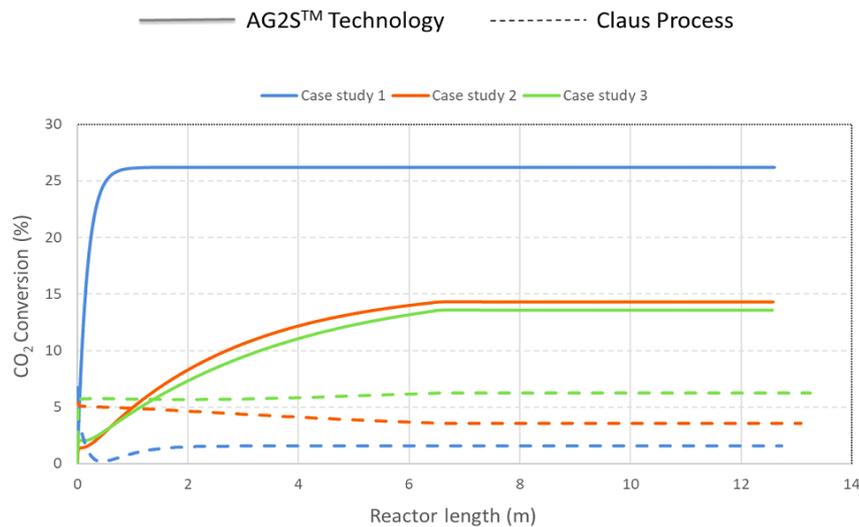


Figure 6. CO₂ conversion in AG2STM technology (straight line) and Claus process (dotted line) in function of carbon dioxide inlet composition and reactor length

Acid Gas to Syngas Greenfield economic assessment

Previous data have demonstrated the functioning of AG2STM in a specific range of applicability. In this section the first basic economic evaluation is performed. Chemical plants are, of course, built to create value, that is – in a medium-term – make profits; thus, the estimates of

the investment required (CAPEX, Capital Expenditure) and of the annual Cash Flows (CF, embedding the Operational Expenditure, OPEX) are needed so that the profitability of any initiative can be assessed. The items to be estimated so as to sum up to the cash flow are the variable costs of production, the fixed costs of production (overall, OPEX) and the revenues from sales, including both main products and by-products considering green-field scenarios (**Table 3**).

In this section, the economic assessment was carried out referring to Chemical Engineering Design [29]. The cost of the plant was established for the CAPEX (which includes also Inside Battery Limits (ISBL), cost of the plants itself, Offsite Battery Limits (OSBL), cost of modification and improvements to be made to the site infrastructure, engineering and construction costs and, working capital and contingency charges); as for the revenues' and costs' estimation, the following parameters have been included: the prices of raw materials such as hydrogen, carbon monoxide; carbon dioxide taxation at 20%; utilities' costs and exploited production capacity.

A study on greenfield case is made in order to have an early stage of the project design. The results show that there is an increase in the revenues greater than the one of investment costs. Even though a lot less impacting on the global level, aiming to reduce CO₂ emissions which come from refineries, the development of the technology as an alternative to the Claus process needs to be considered.

In this section, the estimation of the CAPEX, the revenues and the variable and fixed costs of production are presented. In fact, in this case, the designed process section needs to be built from scratch, so the case needs to be managed as a project on its own. All costs related to the construction of a whole new plant are scaled on the single section and so a project profitability study can be carried [30].

Table 3. Greenfield case fixed costs of production

Fixed costs	UDS/a
Operating Labor	240 000
Supervision	60 000
Direct Salary Overhead	150 000
Maintenance	112 500
Property and Insurance	37 500
Rent of land	52 500
Total	652 500

The added expenditures to be considered are show in **Table 4**. These are fixed costs of production, which means independent of the fact that the plant is producing and from the production volumes themselves.

Considering that the plant needs to be started for the first time, the Working Capital contribution needs to be accounted for. It is assumed to be 5% of ISBL+OSBL and of course, it is added to the CAPEX since it is not an annual cost.

In this analysis, the cost of the furnace and waste heat boiler are taken in account and added to the previously estimated ISBL. The geometry of the thermal furnace, the waste heat boiler and catalytic bed is maintained unchanged.

For the catalyst characteristics, previous work of [31] has been followed, assimilating their catalyst features (bed density and volume of catalyst per volume of reactor) as the standard ones for the Claus process. All calculations made for the case study are reported in **Table 4** together with details of CAPEX contributions.

Table 4. Greenfield investment costs

Greenfield	UDS
ISBL	3 750 000
OSBL	1 500 000
ISBL+OSBL	5 250 000
Contingency	375 000
CAPEX	5 625 000
Working Capital	262 50

The total ISBL results to be 3 750 000 UDS with 1 - 150 000 USD to be accounted for depreciation. This cost appears to be very low and so the greenfield case very promising. All costs and revenues for the study are resumed in **Table 5**.

Table 5. Cost and revenues for CO₂ price equal to 20 \$/ton

Revenues		UDS/a
	S ₂	2 078 080
	H ₂	424 290
	CO	137 040
	CO ₂ taxes	105 900
	Total	2 745 310
Variable costs		
	Steam	973 200
	O ₂	480 000
	Electricity	95 760
	Cooling water	46 800
	Total	1 595 760
Fixed costs	Total	652 500
CAPEX	Total	5 890 000 UDS

The CO₂ abatement, the syngas production and the exploitation of this promising technology in a greenfield case were considered. The greenfield results allow to certainly state that investment was worth taking.

CONCLUSIONS

This work investigates an inventive solution for potential improvements of petrochemical/power plants performance: Acid Gas to Syngas™ technology. Such a synthesis route, from thermodynamics and kinetics studies, appears feasible and promising from technological standpoint. The development has been described using experimental and industrial data, together with an efficient numerical calculation, in order to carry out technical and economical evaluations of a possible feasibility and process utilization. A wider range of acid gas

inlet compositions were investigated: in particular feed with higher carbon dioxide content provided by Nanjing (China) (44 mol %), or the Mesaieed (Qatar) (25 - 9 mol %) industrial plants in order to analyze the effectiveness of Acid Gas to Syngas™ (AG2S™). Results stated that the optimization of all the sensitive parameters (fast quench, low injection of oxygen, good ratio of reagents, inlet temperature) greatly improves the sustainability of the process in terms of quality of syngas produced, limiting, in the meantime the emissions. The economic analysis shows that Capex and Opex results of the greenfield case looks to be very promising for a pilot plant setup. Future analysis spectrum could lead to considering technological applications not only limited to the SRU of refineries; an example could be the direct methanol production or urea synthesis made with this new process route.

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NOMENCLATURE

Abbreviations

AG2S™	Acid Gas to Syngas™
CAPEX	Capital Expenditure
CCS	Carbon Capture and Storage
ISBL	Inside Battery Limits
OSBL	Offside Battery Limits
RTR	Regenerative Thermal Reactor
SRU	Sulfur Recovery Unit
TR	Thermal Reactor
WHB	Waste Heat Boiler

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