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Techno-economic feasibility study of Acid Gas to Syngas (AG2S^{TM}) technology applied to oil refinery

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The novelty of AG2S^{TM} (Acid Gas to Syngas) technology lies in the capability of producing syngas, a valuable product, from acid gases (H_2S and CO_2), which are refinery by-products. This work aims to propose and indicate the implementation of such technology as a revamping option of the already-running Claus plant. An applicability range based on industrial data by coupling two different software applications, i.e., Aspen HYSYS and MATLAB®. A comparison study between the two processes were developed, choosing some critical parameters (i.e., furnace inlet temperature, flame temperature, sulfur recovery efficiency, ratio of H_2S and CO_2 in the feed). The significance of introduced innovations is highlighted, at a technical, economic and environmental level. Due to complete recycle of H_2S, relevant reduction of CO_2, and syngas production the new technology appears to lean toward environmental and energy improvements and it could be integrated, without major investments, into existing systems, significantly increasing their performance.

1. Introduction

Worldwide, around 95,2 million barrels of oil were extracted daily in 2019. All this amount of oil must be treated and processed to satisfy the market requirements (Gani et al. 2020). However, independently from the different final products, refinery generates wastes like hydrogen sulfide (H_2S), extremely toxic and corrosive gas with no economic value (De Crisci et al. 2019), and carbon dioxide (CO_2), a greenhouse gas having negative effects on the ecological and environmental system, so both must be treated (Boot-Handford 2014). Today the biggest challenge is to combine the growing global demand for energy with the exploitation of sustainable materials to generate it. The limited availability of the primary carbon source, such as oil, is at the centre of discussions. While the other fossil resources, coal and natural gas, are available in much greater quantities, their exploitation inevitably leads to the emission of carbon dioxide into the atmosphere. In fact, the critical role CO_2 has in global warming is well known and it's gaining more and more attention in mass and global media concerns. Le Quéré et al. (2012) pointed out that 87% of human carbon dioxide emissions come from the combustion of fossil fuels and, arranging data from other sources (Olivier et al. 2014), the anthropogenic carbon emissions are estimated to be 36.1 Gtons per year (Friedlingstein et al. 2014). Its use would be the most direct way to collect nature's carbon resources, without the bypass by biomass or fossil resources, and would close the carbon cycle most efficiently, so the development and implementation of carbon capture technologies are fundamental to mitigate the growing global CO_2 emissions (Mikkelsen et al. 2010). In the last years, there was an increase in the need for further lowering the amount of sulphur in products from crude oil, to comply with the new plants and emission regulation. H_2S abatement is mandatory due to its noxious nature. The emergence of new approaches and technologies for greater sulphur removal is expected to increase the volume of generated acid gases, in the by-product streams of various desulfurization units. Claus process is the most diffused, well-known and deeply studied process that allows recovering, at the same time, sulphur and thermal energy from acid gases (Taylor et al. 2017). The new proposed technology (Bassani et al. 2016) exploits the amount of CO_2 for the production of syngas (AG2S™ – Acid Gas to Syngas) without any use of hydrogen or costly reducing agents; in fact, another emission, H_2S, is used as a reducing agent. This is an attractive alternative since 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 main reaction, characteristic of the new Claus process, is the regenerative thermal oxy-reduction between H_2S and CO_2, according to the following stoichiometry:

$$2H_2S + CO_2 \rightarrow H_2 + CO + S_2 + H_2O \qquad (1)$$

This reaction is possible when both reagents are in co-presence (i.e. natural gas, coal, shale oil&gas, biomass, biogas). 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 for use as a fuel in gas engines. The aim of this work is to implement AG2S^{TM} as a revamping of the already-running Claus plant, located in China, and to show its industrial feasibility and sustainability at technical, environmental and economic level.

2. Modelling and Simulation tools

In this section, processes descriptions and computational tools were given.

The simulations were realised by coupling Aspen HYSYS® a market-leading process modelling tool for conceptual design, optimization, and performance monitoring, with MATLAB®, in order to realise a complete plant model, able to manage the recycle of unconverted acid gases. The revamping of the existing Claus plant was made by modifying some of the current used unit operations, in particular the thermal furnace, which must be completely redesigned from the constructive point of view. The new design of the reactor consists in a regenerative thermal reactor (RTR), that exploits two different mechanisms: the thermal cracking of H_2S and the oxy-reduction of H_2S by CO_2 at high temperature. In the entire technology the main unit operations were divided and modelled in three sections: Thermal section, consisting of the regenerative thermal reactor (RTR), Catalytic section and Amine Gas Treating Unit (AGTU), for removing acid gas as reported in Figure 1.

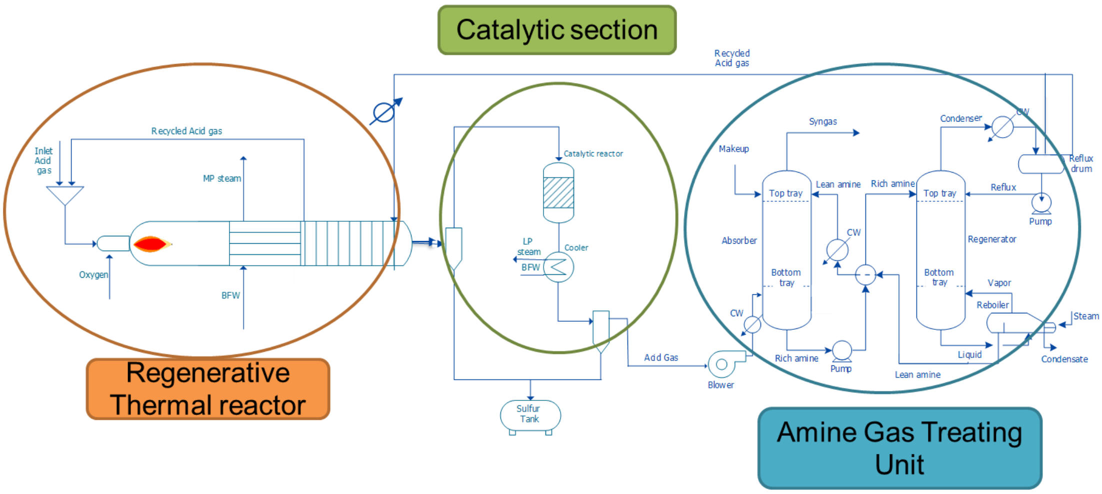

Figure 1. AG2S^{TM} technology - process flow diagram

In the new plant fresh reactants (CO_2 and H_2S coming from upstream plants, assisted by air or oxygen) are injected into the RTR along with recycled reactants; recycle is not necessary for the thermal oxy-reduction, but it is essential for improving self-sustainability of the plant from process standpoint, that is, for reduction or elimination of exhausts. Since RTR reaction is activated at high temperature only, reactants can be fed in either pre-mixed or un-mixed mode. The recycle stream must be pre-heated to avoid that the cold inlet feed in RTR quenches the oxy-reduction reaction. For preheating the feed, recycle stream temperature is raised by an in-line burner, where natural gas or H_2S are combusted by means of an injection of oxygen or air. 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) was installed just at outlet of RTR chamber for quenching the reactions. The amount of sulfur allotropes can be affected by reactor conditions (i.e., gas stream composition and equivalence ratio) studied by Selim et al. (2013) for this reason the distribution of various sulphur allotropes as a function of temperature, at thermodynamic equilibrium, were also considered. The aim was to build a correct model to replicate the real outputs of the process and, also, to compare the performance with the Claus process. For the analysis and the simulation, a real Claus plant based in Nanjing (China) was selected as a case study. For the accuracy of the model, the thermal reactor is exploited by DSMOKE software, developed using a detailed kinetic scheme developed by Manenti et al. (2013). The layout was then implemented and simulated in Aspen HYSYS® and MATLAB® was chosen to interface and integrate DMOKE code within Aspen HYSYS®, in order to include a detailed kinetic scheme in non-ideal reactor models. |The inlet compositions for both processes are reported in Table 1.

Table 1. Inlet composition stream for two processes

	Claus	AG2S^{TM}
Flowrate (kg/h)	4230	5753
Composition (% molar)		
H_2S	0.9055	0.7951
H_2O	0.0612	0.0726
CO_2	0.0452	0.1253

3. Results and discussion

The temperature profiles in the two processes, along the dimensionless length, are reported in Figure 2. In the chamber, SO_2 net rate is almost zero in the AG2STM, while, in Claus process, it was produced abundantly, as it can be seen by the comparable consumption rate of H_2S and SO_2. In fact, the main consumption of hydrogen sulfide in the Claus process is through the reaction of these species. In the AG2STM, even though the H_2S consumption rate is slightly lower than the Claus case, a relevant CO2 consumption can be appreciated as well. As it could have been suspected by analyzing the previous trends, an important contribution to the global reaction is given by the reverse water gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). That is confirmed by the trends of the reaction rates, in fact for the four species involved in the reactions the trends are coupled and almost symmetric. The slight deviation from the symmetry given by hydrogen and water rates is due to the contribution of the oxy-reduction reaction of the AG2S^{TM} that consumes CO_2 and H_2S to give back H_2 and CO (together with elemental sulfur and water). It is to be noticed that the low oxidizing conditions of the environment allow the global production of H_2 and CO. A little amount of produced SO_2 is then reacting through the Claus reaction to further consume H_2S.

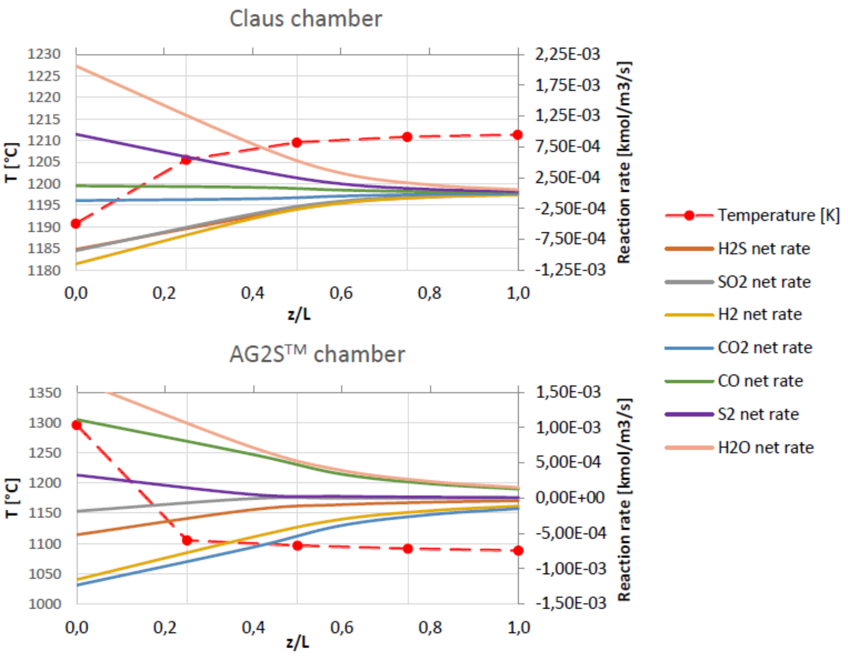

Figure 2. Reaction rates in the furnace chamber: Claus process vs AG2S^{TM} technology

The comparison between the outputs of both processes has been carried for the case study as well. As Table 2 shows, in the revamped case the hydrogen production is enhanced, almost tripled. In particular, almost a quarter of the inlet H_2S moles are converted to H_2. Moreover, even though the conversion per pass is reduced, the global conversion is almost 100% thanks to the recycle. The real value is 99.9% due to traces of H_2S in the separated liquid sulphur and in the resulting syngas, but the performance is comparable to the one obtained by the combination of Claus and TGTU (97.14%) The sulphur production is, of course, the same while the net steam production in the waste heat boiler is reduced. It's partly due to the use of part of the produced steam in the pre-heating section and mostly due to the choice of a different energy recovery method (economizer). Syngas production can largely compensate this reduced steam production though.
The analysis takes into account also CO_2 production and consumption. So, from the carbon dioxide production in the Claus process, with this new technology, it moves to a conversion of 93% of the inbound CO_2. As mentioned, the new technology allows to produce syngas, the results show the ratio of hydrogen and carbon monoxide equal to 1.51. As it can be noticed, due to its purity, the produced syngas can be considered of great economic value due to the further application (i.e. methanol synthesis). Referring to the results performed the revamping to the new technology has many advantages.

Table 2. Comparison between case study and revamping case study

	Claus Process	AG2S^{TM}
Outlet H_2 (kg/h)	18.94	52.62
Sulfur recovery (mol/mol)	97.14%	99.90%
H_2 produced/H_2S inlet (mol/mol)	9.10%	25.40%
Inlet CO_2 (kmol/h)	9.04	9.04
Outlet CO_2 (kmol/h)	14.44	0.63
CO_2 production from fuel gas combustion (kmol/h)	5.40	0.0
CO_2 conversion (kmol/h)	-59.73%	93.00%
Syngas production (kmol/h)	0.00	65.30

4. AG2S^{TM}: Economic and Financial Assessment

The economic and financial performance of both a revamping and green-field initiative have been assessed through Discounted Net Present Value (DNPV) and Pay Back Time (PBT). Given the nature of the situation (feasibility study), the needed input information (specifically, CAPEX, CAPital EXpenditure and OPEX, OPerational EXpenditure) has been estimated following to a well-known and widely used approach as in Towler et. al. (2013), supported by Aspen HYSYS® for the estimation of the cost of the non-traditional equipment.
The revamping to AG2S^{TM}, even though extremely promising because of the significant number of existing plants potentially being involved and because of the achievable reduction in CO_2 emissions, currently appears to be not economically sustainable (the OPEX have resulted higher than the revenues, thus DNPV<0 and no PBT). The added value of this option comes from the syngas sales and the CO_2 abatement, which today are not enough to balance the pertinent OPEX and CAPEX.
The AG2S^{TM} greenfield case is reported to have overall a greater increase in revenues than in costs (both CAPEX and OPEX). Therefore, as an option to significantly reduce the CO_2 emissions coming from refineries, AG2S^{TM} is worth being considered as a viable alternative to the Claus process. The economic and financial assessment has been performed in a sensitivity analysis mode, keeping into account: the current variability and likely uncertainty in the next years of the prices of the reactants and products, as well as the costs of the utilities, and the streams flowrate which could vary impacting the investment on a global level. In particular, a preliminary sensitivity analysis allowed to clarify that the major impact derives from the steam consumption, mainly due to the great flowrate involved. The DNPV and the PBT were then assessed, by mapping them in three different scenarios (Figure 3), dependent on the estimated values of CO_2 taxation, moving from 50 to 75 $/ton (Gupta et al. 2016; Fiscal Policies for Paris Climate Strategies 2019) and on a variation of sulfur market (http://www.sunsirs.com.). Also, the PBT can benefit from reduction (10% in Figure 3) in steam consumption, and, with a more efficient heat exchange network, the reduction might be increased even more. Moreover, taking into account that in a refinery there can be an excess of steam, since it is a side product of other processes (Macedonio et al. 2012), its cost can be reduced to almost zero completely changing the global balance; overall this would significantly support the best case.
All in all, the greenfield application benefits from a significant income due to sulphur recovery and carbon dioxide abatement; In particular, the best scenario highlights a promising situation, with a very positive DNPV, and an

acceptable (depending on the investors/sponsors) PBT. The details about costs and revenues are available under request.

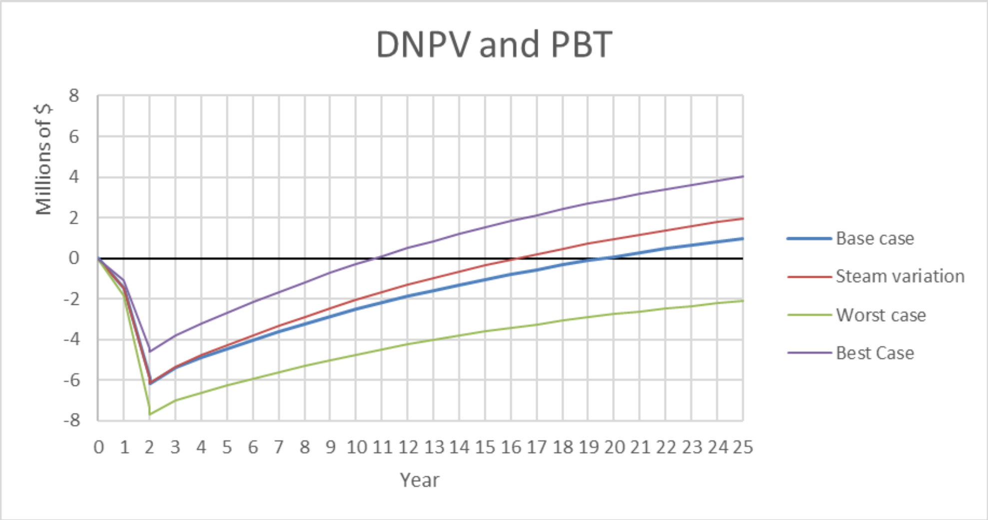

Figure 3. Economic and Financial Assessment – Greenfield case. The diagram reports the Discounted Net Present Value (DNPV) cumulation over time; its intersection with "x" axis results in the Pay Back Time (PBT)

5. Conclusions

This paper proposes and illustrates the sustainability and feasibility of the revamping for a standard Claus plant at AG2S ™ and a comparative techno-economic comparison between the traditional technology (hereinafter, Traditional Technology) for the Sulfur Recovery Units, SRUs) and the new Acid Gas to Syngas™ (AG2S ™) technology.

The results present the effectiveness and environmental benefit by AG2S™ technology. The basic idea is to reduce the emissions of H_2S and CO_2 to exploit the oxidizing capacity coupling those species with increasing production of syngas. The most important results are the lower emissions of CO_2 with respect to the traditional Claus process. Moreover, it is proved that a high sulfur content charge allows a higher reduction of CO_2 emissions. This solution leads to other advantages like the possibility to exploit feed with higher carbon dioxide content such as the Nanjing industrial plants. The highlight results, strongly, point that the technology enhances and encourages the reuse of CO_2 in line with current European regulations and greatly improves the sustainability of the process thanks to the limited emissions. The CO_2 emission abatement will surely gain interest in the next years, as the production of hydrogen (or syngas) from different sources. The results have illustrated that the novel process is also very interesting and economically appealing.

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