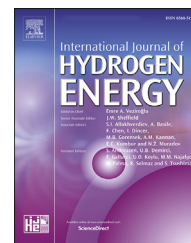


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## Sorption Enhanced Water Gas Shift for H<sub>2</sub> production using sour gases as feedstock

Andrea Bassani<sup>a</sup>, H.A.J. van Dijk<sup>b</sup>, P.D. Cobden<sup>b</sup>, Giorgia Spigno<sup>a</sup>,  
Giampaolo Manzolini<sup>c,\*</sup>, Flavio Manenti<sup>c</sup>

<sup>a</sup> Univesità Cattolica del Sacro Cuore, DiSTAS – Department for Sustainable Food Process, Via Emilia Parmense 84, 29122 Piacenza, Italy

<sup>b</sup> TNO, Westerduinweg 3, 1755, LE Petten, the Netherlands

<sup>c</sup> Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy

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### ABSTRACT

Even though hydrogen is considered the future of energy carrier, it is still produced from fossil fuels therefore with no benefits for the CO<sub>2</sub> emission reduction. This paper discusses an innovative concept for hydrogen production which combines the Acid Gas to Syngas (AG2S™) concept and the Sorption Enhanced Water Gas Shift (SEWGS) process. The AG2S™ process produces H<sub>2</sub> and elemental Sulfur from H<sub>2</sub>S and CO<sub>2</sub>, then H<sub>2</sub> purification is performed through amine scrubbing. The SEWGS technology is a Pressure Swing Adsorption process where the CO<sub>2</sub> and H<sub>2</sub>S are adsorbed on hydrotalcite-based material. With respect to amine scrubbing, SEWGS takes advantage of a higher operating temperature of 350 °C –400 °C which reduces temperature swing losses, lower regeneration energy and the possibility to recycle the H<sub>2</sub>S while capturing the CO<sub>2</sub>. This study aims at exploring the potential of the SEWGS technology by means of the evaluation of detailed mass and energy balances, showing the potentialities of the AG2S™+SEWGS technologies which more than double the H<sub>2</sub> production efficiency (25.0%) with respect to the amine scrubbing configuration (10.7%). Including the steam production, the overall process efficiency can be higher than 90% which is again more than twice the value of the AG2S™ reference case.

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### Introduction

Hydrogen is one of the most studied energy carriers worldwide as it can replace conventional fossil fuels (coal, oil and natural gas) mitigating greenhouse gases emissions (mainly CO<sub>2</sub>) [1]. One of the main limits to its diffusion is related to both high cost production and lack of infrastructures. With respect to the cost of production, H<sub>2</sub> prices are higher than conventional fossil fuels as the latter are used as primary

source to produce around 96% of hydrogen. Natural gas steam reforming is the most used technology covering 50% of the global production [2,3]. Green hydrogen production (i.e. hydrogen generated by renewable sources) is limited to water electrolysis using photovoltaics or wind energy and it is currently quite expensive [4–6]. Therefore, the only way to make hydrogen economically viable is to identify production routes cheaper than the ones currently available on the market.

\* Corresponding author.

E-mail address: [giampaolo.manzolini@polimi.it](mailto:giampaolo.manzolini@polimi.it) (G. Manzolini).

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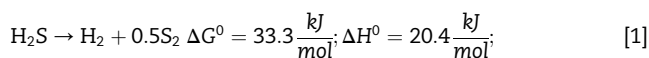
**Nomenclature**

<b>AG2S</b>	Acid Gas to Syngas
<b>HP</b>	High pressure
<b>KPI</b>	Key Performance Indicators
<b>IP</b>	Intermediate pressure
<b>LHV</b>	Low Heating value
<b>LP</b>	Low pressure
<b>MDEA</b>	Methyl Diethanol Amine
<b>PSA</b>	Pressure Swing Adsorption
<b>RTR</b>	Regenerative Thermal Reactor
<b>SEWGS</b>	Sorption Enhanced Water Gas Shift process
<b>WHB</b>	Waste Heat Boiler
$\Delta G^0$	: standard Gibbs free energy
$\Delta H^0$	: enthalpy of dissociation
$H_2$ -yield	Hydrogen production yield
$\eta_{H_2}$	hydrogen production efficiency
$\eta_{overall}$	overall system efficiency

Among the alternative routes investigated in literature for producing hydrogen, one of the most attractive ones consists of using hydrogen Sulfide ( $H_2S$ ) as fuel. Hydrogen Sulfide has a very high LHV (15.2 MJ/kg, 18.9 MJ/Nm<sup>3</sup>) but justifiably banned as feedstock, since Sulfur dioxide is produced during combustion and this is not environmentally acceptable. However,  $H_2S$  is present as a dangerous waste in many industrial activities [7] and fossil fuel sources [8], it represents a serious risk factor in acute and chronic poisoning for workers [9] and need to be processed to avoid emissions.

Interest in hydrogen production from  $H_2S$  dates back in 1984 [10], because of its large presence in some areas as Canada and the Black Sea [11]. However, after 25 years, there is still no commercially viable system.

Several technologies have been proposed for converting  $H_2S$  into hydrogen: thermolysis was one of the first investigated technique for  $H_2S$  splitting, probably because its schematic simplicity which does not however correspond to an operational ease. The following equation summarizes the standard Gibbs free energy and enthalpy of dissociation for  $H_2S$  [12].



The dissociation is carried out at high temperature in the range of 700 °C–1000 °C. A temperature of 700 °C is identified as discriminant between a catalytic or purely thermal  $H_2S$  splitting [7]. Many studies have investigated thermochemical cycles together with the effects of several process parameters [13]. Despite higher efficiency with respect to other  $H_2S$  splitting techniques, this concept increases the plant complexity together with an accurate and demanding management between the different sections. Other processes are based on photocatalytic methods using the electron excitation by solar photons. Several materials have been proposed for  $H_2S$  photocatalytic splitting as CdS/TiO<sub>2</sub> [7], CdS [14] or CdS/Pt [15]. According to Ref. [7], only studies where the photolysis of  $H_2S$  occurs in batch reactors where the catalyst is suspended in a liquid phase or immobilized on a fixed substrate, have been reported. Therefore, a significant

breakthrough is necessary to take this technology to the commercialization level.

The present work investigates a new route for hydrogen production starting from  $H_2S$  and using  $CO_2$  as an oxidizing agent (e.g. reforming reaction) [16,17] and the purification step is performed by an innovative process called Sorption Enhanced Water Gas Shift (SEWGS) [18,19]. In particular, the hydrogen production process called Acid-Gas-To-Syngas (AG2S™) already presented in previous work produces a stream rich in hydrogen and elemental sulfur with unconverted  $H_2S$ ,  $CO_2$ ,  $CO$  and steam [17]. The hydrogen purification is usually performed at ambient temperature by amine scrubbing which is an energy intensive process. In this context, this study aims at exploring the potential of the SEWGS technology. One of the advantages of this technology would be to increase the conversion in the system, while simultaneously decreasing the temperature difference between consecutive process steps, to avoid unnecessary energy loss, e.g. due to condensation. In this work, the hydrogen purification is carried out in the SEWGS where hydrotalcite-based material simultaneously absorbs and separates  $CO_2$  and  $H_2S$  from the hydrogen rich stream. The separated  $H_2S$  can be recycled in the AG2S™ system increasing the hydrogen production while the  $CO_2$  can be stored preventing its venting to the atmosphere. The technology is evaluated from an energy perspective assessing the hydrogen production efficiency for different considered lay-outs. The interest for the combination of these two processes relies on the large presence of syngas with  $CO_2$  and  $H_2S$  as in the gasification processes, refinery processes and in natural gas reservoir in the Black Sea/Caspian areas.

This work is carried out within the European H2020 STEPWISE project, in which the Sorption Enhanced Water-Gas Shift (SEWGS)  $CO_2$  capture technology is brought to TRL6 by means of design, construction, operation and modelling a pilot installation in the Iron and Steel industry using actual Blast Furnace Gas (BFG). This advanced  $CO_2$  removal technology makes use of regenerative solid adsorbents. The  $CO_2$  removal section is comprised of a single stage pre-shift section to perform the bulk of the  $CO$  conversion to  $CO_2$  and  $H_2$ , followed by SEWGS unit consisting of multiple columns operating in pressure-swing mode [20,21]. The solid adsorbent interacts with  $CO_2$  and acid gasses like  $H_2S$ , producing a decarbonised and desulfurized fuel gas, and is regenerated at low pressure using a steam purge producing a  $CO_2$  stream for capture or utilisation.

The paper is organized as follow: [section AG2S™ technology and reference case](#) describes the AG2S™ technology and the reference case, SEWGS technology is introduced in [section SEWGS technology and application to sour streams](#) together with the proposed lay-out. [Section Methodology](#) presents the adopted methodology and the energy results are discussed in [section Results](#). Finally, conclusions and future applications are reported in [Section Conclusions and outlooks](#)

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## AG2S™ technology and reference case

As mentioned in the introduction,  $H_2S$  is a toxic molecule and undesired emissions. The Claus process is the most

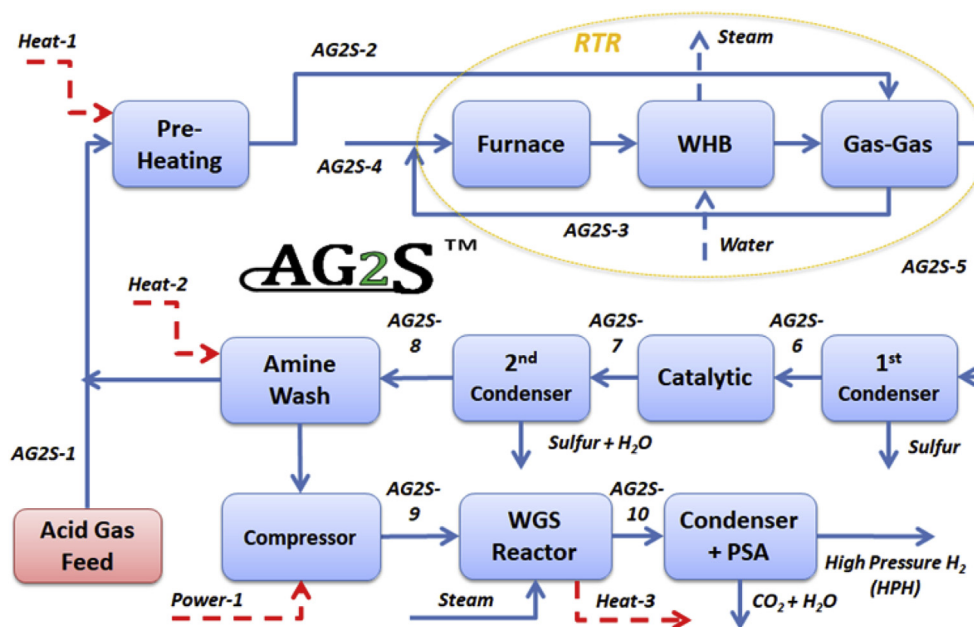
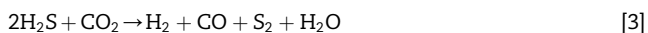


Fig. 1 – Block flow diagram of AG2S™ process.

widespread large-scale technology adopted for the removal of  $H_2S$  as solid sulfur [8]. This process involves several reactions such as oxidation [22] and pyrolysis of  $H_2S$  [23]. The overall global reaction



is a complex radical mechanism with many elementary processes where various reactive systems are coupled by common intermediate radical [24]. However, as reported above, it could be possible to convert  $H_2S$  and  $CO_2$  into syngas according to an oxy-reduction reaction, which takes place in a regenerative thermal reactor:



AG2S™ allows to use energy sources currently still unexploited because of their relevant sulfur content, such as crude oils, natural gases, different coals [25] or geothermal energy [26]. In this paragraph, the overall layout of the novel AG2S™

process is briefly discussed and the main streams with the corresponding thermodynamic conditions are reported. The detailed description and simulation of AG2S™ process are reported in the previous works of Bassani et al. [17,25]. The overall layout of the process is illustrated as block flow diagram in Fig. 1.

The main feature of the plant is the regenerative thermal reactor (RTR), which has a different configuration compared with the typical Claus furnace [27]. RTR is mainly composed by a furnace, a waste heat boiler (WHB) and a heat exchanger (gas-gas). This design allows to recover as much as possible hydrogen from the  $H_2S$  reaching the main goal of AG2S™ process. The key idea is to feed an optimal ratio of  $H_2S$  and  $CO_2$  and to preheat the inlet acid gas before the combustion. In this way,  $H_2S$  pyrolysis produces hydrogen selectively. Indeed, it is convenient to feed the acid gases to the RTR at high temperatures (e.g. 800 °C) in order to reduce the oxygen flow rate required to reach the furnace temperatures (1100–1350 °C).

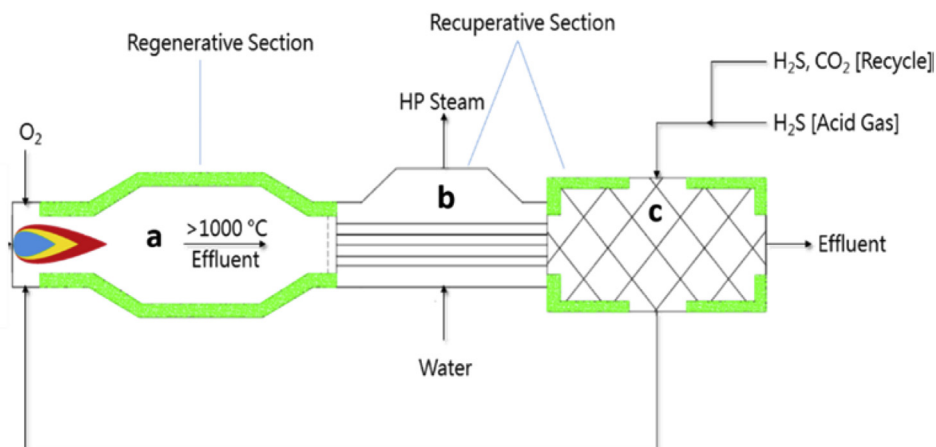


Fig. 2 – Regenerative Thermal Reactor (RTR) configuration.

**Table 1 – Main streams compositions of AG2S™ Process (Base Case).**

	AG2S-1	AG2S-2	AG2S-3	AG2S-4	AG2S-5
Total Mass Flow [kg/h]	6522.16	13330.03	13330.03	1875.00	15205.03
H <sub>2</sub> S [% mol]	74.32	78.25	78.25	0.00	32.57
CO <sub>2</sub> [% mol]	12.82	11.84	11.84	0.00	5.69
H <sub>2</sub> [% mol]	0.00	0.00	0.00	0.00	6.50
CO [% mol]	0.00	0.00	0.00	0.00	3.92
O <sub>2</sub> [% mol]	0.00	0.00	0.00	1.00	0.00
SO <sub>2</sub> [% mol]	0.00	0.00	0.00	0.00	0.02
S <sub>x</sub> [% mol]	0.00	0.00	0.00	0.00	14.79
COS [% mol]	0.00	0.00	0.00	0.00	1.45
CS <sub>2</sub> [% mol]	0.00	0.00	0.00	0.00	0.05
H <sub>2</sub> O [% mol]	11.15	9.02	9.02	0.00	35.01
Light Hydrocarbon [% mol]	1.55	0.76	0.76	0.00	0.00
Temperature [°C]	55.50	161.53	779.20	97.00	350.00
Pressure [bar]	1.50	1.50	1.50	1.50	1.50
	AG2S-6	AG2S-7	AG2S-8	AG2S-9	AG2S-10
Total Mass Flow [kg/h]	12103.61	12103.61	8410.55	1186.24	2897.67
H <sub>2</sub> S [% mol]	36.48	38.16	57.26	0.00	0.00
CO <sub>2</sub> [% mol]	6.37	8.05	12.09	19.73	18.53
H <sub>2</sub> [% mol]	7.28	7.28	10.93	48.28	30.10
CO [% mol]	4.39	4.38	6.58	29.08	1.25
O <sub>2</sub> [% mol]	0.00	0.00	0.00	0.00	0.00
SO <sub>2</sub> [% mol]	0.03	0.00	0.00	0.00	0.00
S <sub>x</sub> [% mol]	4.55	4.59	0.00	0.00	0.00
COS [% mol]	1.62	0.00	0.00	0.00	0.00
CS <sub>2</sub> [% mol]	0.06	0.00	0.00	0.00	0.00
H <sub>2</sub> O [% mol]	39.21	37.52	12.98	2.89	50.11
Light Hydrocarbon [% mol]	0.00	0.00	0.00	0.00	0.00
Temperature [°C]	182.00	198.00	60.00	350.00	213.00
Pressure [bar]	1.50	1.50	1.50	21.00	21.00

Therefore, the oxygen stream is much lower than the typical oxygen provided to the Claus processes and the H<sub>2</sub>S potential for pyrolysis is completely exploited. As in the traditional Claus process, the released heat is recovered generating high pressure steam in a Waste Heat Boiler (WHB). The RTR design is reported in Fig. 2. The WHB and recycle pre-heating equipment could be considered a portion of the RTR because they play a key role in the regenerative process.

The catalytic reactor configuration is the typical one of the Claus process [28], but the reactions involved are mainly the hydrolysis of carbon disulfide (CS<sub>2</sub>) and carbon sulfide (COS) instead of the Claus reaction, due to the low amount of SO<sub>2</sub> into inlet stream



The removal of COS and CS<sub>2</sub> are performed with almost

100% conversion and the hydrolysis reactions take place on gamma-alumina at mild conditions.

This process configuration takes advantage by the unreacted acid gases recycle. It is important to underline that, in this work, water gas shift reactor and SEWGS (which is Pressure Swing Adsorption together with the water gas shift reaction and CO<sub>2</sub> adsorption) are added in order to produce pure hydrogen. In this way, the energy improvements due to the integration of the SEWGS technology to the AG2S™ process will be verified basing on the same amount of pure hydrogen produced. Table 1 reports the main streams compositions with the corresponding thermodynamic conditions, while Table 2 and Table 3 report the steam produced or consumed respectively by the process. The names of the streams relate to names reported in Fig. 1. The inlet stream composition could be a typical composition of acid gas stream coming from refinery process (e.g. hydro-desulfuration process) [29]. The mass flow rate of H<sub>2</sub>S is about 118 ton/day, that is a typical value of H<sub>2</sub>S treated in a traditional Claus plant [30]. The inlet ratio between the H<sub>2</sub>S and CO<sub>2</sub> is equal to 5.8. The

**Table 2 – Steam produced in AG2S™ process (base case).**

	WHB	1st Condenser	WGS
Mass Flow [kg/h]	6512	7463	516
Temperature [°C]	265	170	180
Heat [kW]	3016	4297	292.3

**Table 3 – Steam consumed in AG2S™ process (base case).**

	Pre-Heating	Amine-Wash
Mass Flow [kg/h]	1088	30260
Temperature [°C]	180	150
Heat [kW]	616	17950

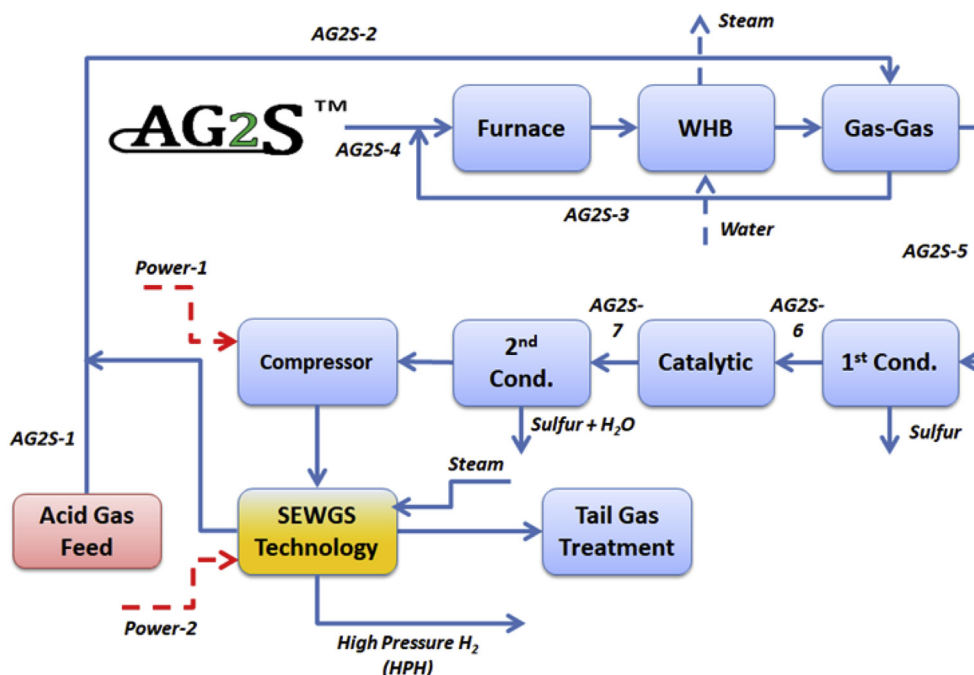


Fig. 3 – Block flow diagram of AG2S™ + SEWGS.

final hydrogen produced is 48.1 kmol/h (i.e. 96.2 kg/h) at 21 bar and so is already compressed for downstream operation or other processes. Pressure was set to be consistent with the SEWGS case and power consumed by the compressor to reach that pressure is equal to 261 kW, calculated using Aspen HYSYS. Moreover, it is important to underline that the scale effect will be not investigated in this work. Indeed, the comparison between the traditional and the novel process will be based only on thermodynamic considerations.

### SEWGS technology and application to sour streams

The Sorption-Enhanced Water Gas Shift (SEWGS) process has been developed in the first instance for use in pre-combustion power production with carbon capture, based on both natural gas [31] and coal [19] via gasification, as input fuels. It can, however, be applied for decarbonization of any type of fuel gas or syngas. It is currently being demonstrated in the European Projects STEPWISE [32,33] and FReSMe project [34] for carbon capture from iron and steel process gases, for use in electricity and methanol production respectively. At full-scale, multiple reactors are filled with an anionic clay, hydrotalcite that is promoted with  $K_2CO_3$  [35]. In turn, each reactor is exposed to the reactant gases,  $CO_2$  is removed by adsorption, CO is converted to  $CO_2$  and  $H_2O$  with any steam present via the WGS reaction, and  $H_2S$  is also adsorbed [21]. The  $CO_2$  capacity of the sorbent slightly drops at increased  $H_2S$  feed content [21]. As  $CO_2$  and  $H_2S$  are both acid components, some sort of competition for sorption capacity can be imagined. Nevertheless, the remaining capacity for  $CO_2$  is adequate to design a cycle where high removal rates of both  $CO_2$  and  $H_2S$  are possible. Once the

sorbent is saturated with  $CO_2$  and  $H_2S$ , the pressure is dropped and the  $H_2S$  and the  $CO_2$  can be regenerated sequentially by the addition of relatively small amount of steam [36,37]. A typical PSA-like cycle is used to produce a constant flow of  $H_2$  product, and acid gas products. While, in standard WGS, the reaction to  $H_2$  product is limited by thermodynamic properties, in the SEWGS, as  $CO_2$  and  $H_2S$  are removed from the gas, high conversion of CO can be reached even at high temperatures. It must be outlined that the sorbent is active for the WGS reaction, and is active for hydrolysis catalysis. Any COS &  $CS_2$  will be hydrolysed to  $H_2S$  in the presence of steam, according to the thermodynamic equilibrium expectations, as has also been shown in experimental studies. This allows for an easier integration within multiple processing schemes, avoiding intermediate cooling and reheating. Previous work [37] and the STEPWISE project [38] confirmed in the pilot plant in Lulea (Sweden) the sorbent stability to deal with  $H_2S$  and  $CO_2$ .

### SEWGS application to AG2S™

The adoption of SEWGS Technology for  $H_2$  production from acid gases is reported in Fig. 3. The process coincides with the traditional one up to the 2nd sulfur condenser, after which a syngas compressor is necessary to take the syngas to the SEWGS operating pressure (16–21 bar). The pressure is set to achieve the syngas temperature of 350 °C and 400 °C which is the optimal operating conditions for the WGS reaction and  $CO_2/H_2S$  adsorption. The SEWGS process produces three streams at the outlet: high pressure hydrogen which can be sent after cooling (recovering Intermediate-Pressure and Low-Pressure steam) to the final purification and compression unit (i.e. an adsorption bed) which takes the  $H_2$  purity up to

99.999% [39]. A H<sub>2</sub>S rich stream obtained during the first regeneration part which can be recycled back to the RTR reactor. Since the H<sub>2</sub>S is already at high temperature, the pre-heater necessary in the reference case can be neglected in this configuration with cost savings. The last stream is a CO<sub>2</sub> rich stream. The latter is partly used for the rinse step (performed at around 6.5 bar, therefore it must be compressed), partly recycled back to RTR to set the optimal ratio between H<sub>2</sub>S a CO<sub>2</sub> and the remaining part can be sent to the tail gas treatment unit. With respect to the conventional AG2S™ configuration, the CO<sub>2</sub> and H<sub>2</sub>S separation at high temperature reduces the syngas temperature swing, recycles the unconverted H<sub>2</sub>S and saves the acid gas pre-heating. As already mentioned, the combination of AG2S™ and SEWGS technology leads to a better management of recycle ratio between H<sub>2</sub>S and CO<sub>2</sub> than amine scrubbing which generates one single stream with both H<sub>2</sub>S and CO<sub>2</sub>: SEWGS concentrates the H<sub>2</sub>S and CO<sub>2</sub> in two different streams during the regeneration step whose composition and flowrate can be tuned to optimize the H<sub>2</sub> yield. However, in order to properly compare the traditional process and the combined one in terms of energy yield, the composition of the recycled acid gas stream are considered same in both cases. In this way, recovering heat form the stream “AG2S-2” (see Fig. 2), it is possible to have the same stream condition reported in Table 2. The steam and the power consumptions by SEWGS will be analyzed and described in the next sections.

## Methodology

Before starting to analyze the model related to AG2S™ process, the tools and the instruments (DSMOKE, Matlab and Aspen HYSYS) adopted in this work are briefly introduced.

### DSMOKE

DSMOKE software is a simulation tool whose targets is to simulate different kinds of ideal reactors using a detailed kinetic scheme [40]. Simulations consider different chemical-physical properties including composition, temperature, pressure, conversion, reaction heat and exchanged heat. This software requires a kinetic scheme compilation, through an interpreter, with thermodynamic data that returns a kinetic model in the simulation program required format. DSMOKE has a simple interface for reactors network construction and also a sensitivity analysis tool very useful to investigate which reactions have an important contribution on the simulation results. This computational tool uses standard material and energy balances of CSTR and PFR reactors [41].

### MATLAB

MATLAB, MAtrix LABoratory, is a multi-paradigm numerical computing environment and fourth-generation programming language developed by MathWorks. MATLAB® allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including C, C++,

Java, Fortran and Python. One of the main key features of this simulation software are the possibility to Interface with C/ C++, Java®, .NET, Python, SQL, Hadoop, Microsoft Excel and Aspen HYSYS;

### Aspen HYSYS

Aspen HYSYS is a commercial user-friendly package used to simulate chemical plants. Thanks to a simple graphical interface, the users can enter lots of unit operations, like columns, tanks, reactors, separators, etc., already implemented from the point of view of the mathematical model and of the numerical solution. This simulation tool was chosen because, in addition to being widely used at the industrial level, it allows to be faster in the simulation of those unit operations that are already studied and modelled. It is also possible to integrate external simulation tools, for example DSMOKE, into Aspen HYSYS. Indeed, the principal reactor of AG2S™ process is simulated using DSMOKE which is integrated within Aspen HYSYS using Visual Basic programming language or MATLAB. This allows also to integrate a detailed kinetic scheme that is not directly included in aspen HYSYS.

### Process modelling

The models of the principal units were already presented and analyzed in-deep in some previous works of Bassani et al. [26,41]. However, a briefly description is provided for completeness. The Peng-Robinson-Styjek-Vera (PRSV) equation of state is used for the entire process except for RTR, that is simulated using DSMOKE, and the amine wash section, where the amine package included in Aspen HYSYS® is adopted [42]. As already mentioned, the RTR is similar to the Claus one, but redesigned from the constructive point of view (Fig. 2). For these reasons, the RTR could be simulated as:

- > Furnace: Adiabatic plug flow reactor using DSMOKE with detailed kinetic;
- > WHB: Non-Isothermal plug flow reactor using DSMOKE with detailed kinetic;
- > GAS-GAS: Heat exchanger in Aspen Hysys

It is important to underline that the detailed kinetic scheme selected is made up of three different subsets of reactions that describe the kinetic of Carbon, Sulfur, and Nitrogen. This allows also to predict the formations of minor species such as the organosulfur compounds like COS and CS<sub>2</sub>. The validity of this kinetic scheme was also proved with the comparisons with the experimental data provided by El-Melih et al. [16] and reported Fig. 4. Melih et al. analyzed and discuss the effect of a plug flow reactor temperature on the syngas recovery from acid gases at experimental laboratory scale.

These experimental data further prove the validity of the AG2S™ process at the operating conditions of study. Indeed, it is possible to observe that the conversion of CO<sub>2</sub> in the reactor is about 30% in the RTR. Given that the experimental data may have intrinsic errors that cannot be verified due to the absence of other experimental data available in literature about H<sub>2</sub>S–CO<sub>2</sub> reaction, the discrepancies between numerical and

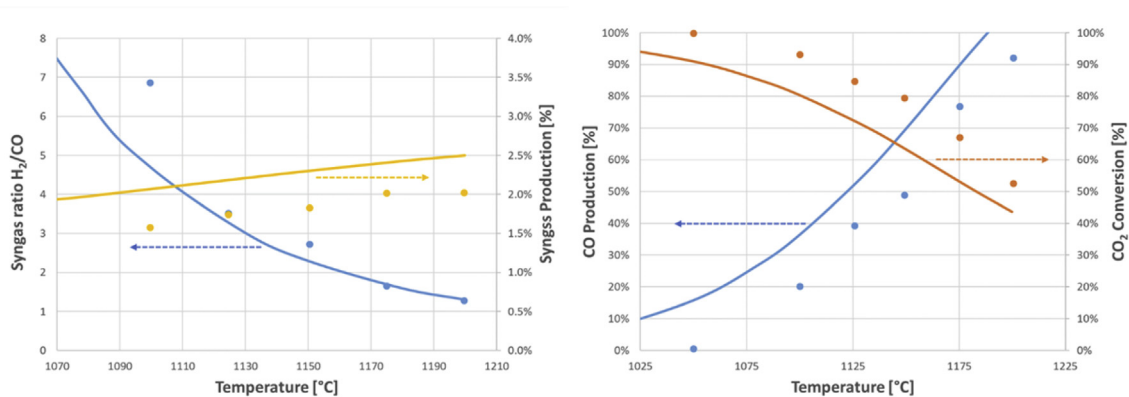


Fig. 4 – Effect of reactor temperature on syngas production and ratio (3% H<sub>2</sub>S/2% CO<sub>2</sub> diluted in 95% N<sub>2</sub>). Dots are experimental data [16] and the lines are the numerical results.

experimental results in Fig. 4 could be mainly due to gaps in the detail kinetic scheme. Indeed, the latter was tested and validated on real data of the traditional Claus process [43], where H<sub>2</sub>S oxidation is the main reaction that dominates over all the others. AG2S™ process works with a lower amount of oxygen and so other reactions (e.g. H<sub>2</sub>S pyrolysis), cannot be neglected. For instance, hydrogen production which comes from pyrolysis of H<sub>2</sub>S could be underestimated as reported in the previous work of Manenti et al. [40]. In Fig. 4, it is possible to notice an overestimation in the production of CO, which leads to an underestimation of outlet H<sub>2</sub>/CO ratio. The total amount of syngas produced is slightly overestimated, and this could lead to a slightly overestimation of hydrogen produced. However, it is necessary to consider the fact that the temperatures related to these experimental analyses are the typical one of the thermal section of the RTR and so the effect recombination reactions of CO and H<sub>2</sub>S, that occurs at the operating conditions of WHB, are not considered. These reactions allow to correctly predict the outlet composition in the traditional Claus case [43] and so partially balance the overestimation of the CO in the thermal section. For these reasons and due to the similarity between RTR and Claus furnace both

at technical and simulation level, it is possible to affirm that the kinetic scheme, although applied to an innovative process, can reasonably foresee a real industrial application of AG2S™.

The catalytic reactors of AG2S™ technology are the same of the traditional Claus process. Indeed, the aim of the reactors is to convert the remaining amount of SO<sub>2</sub> through the Claus reaction (6) and to convert COS and CS<sub>2</sub> into H<sub>2</sub>S and CO<sub>2</sub> by means of hydrolysis reactions (4), (5). The simulation of the catalytic reactor is usually carried out using conversion reactor, with a conversion factor of 100% for each reaction. Finally, the amine washing section is simulated entirely through HYSYS software, thanks to a template already existing in the commercial package. One of the most common configurations of an amine treatment unit is composed of a single absorption column, one regeneration column and all related equipment, such as pumps, heat exchangers and filters (Fig. 5).

The acid gas is fed to the bottom of the absorption column where is absorbed in the solvent and reacts with the amine, in a chemical-physical equilibrium. The amine solution, which is sulfur rich, leaves the absorption column and passes into a flash vessel, where its pressure is reduced to allow the

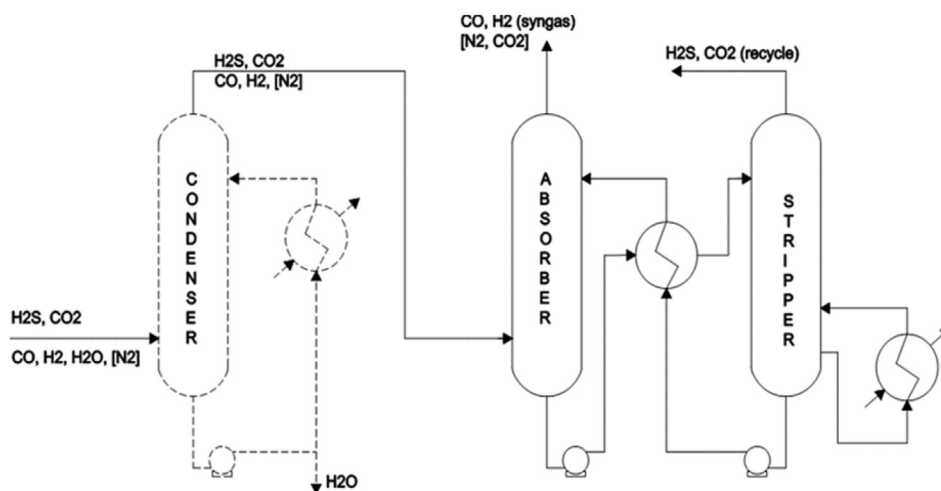


Fig. 5 – Simplified PFD of the amine gas treating unit.

instantaneous vaporization of the soluble hydrocarbons and the removal of the condensed hydrocarbons. Upon leaving the vessel, the rich amine passes through a heat exchanger where the liquid is preheated using the poor amine solution as hot stream and reaches the top of the regeneration column. The heat supplied by the reboiler is needed to bring the rich amine to the boiling temperature, to break the chemical bond between the acid gas and amine, and finally to produce a stream able to reduce the partial pressure and to allow the acid gas stripping from the solvent. The stripping acid gas is recycled to RTR and the poor amine hot stream is recirculated from the reboiler to the absorber tower. For this work, it is decided to use the methyl diethanolamine (MDEA) for its industrial application and its specific selectivity to hydrogen sulfide [44]. Finally, the industrial scale WGS reactor usually consists of a High Temperature Shift (HTS) adiabatic stage followed by a Low Temperature Shift (LTS) with an intermediate cooling. The equilibrium reactors in Aspen Hysys are selected in order to simulate these reactors [22].

So far, the SEWGS concept was firstly applied to CO<sub>2</sub> capture in Integrated gasification Combined cycle (coal fueled) [19,45] and in steel plant [46] where the main purpose was to separate the CO<sub>2</sub> for storage, but more recently it was also considered for sour gas removal [47]. The SEWGS modelling was performed by a proprietary tool of ECN part of TNO which has been developed over the last 10 years [36,48,49]. The model, which is an equilibrium model with terms of mass transfer resistances incorporated, was validated by TGA and cycle measurements in the six columns test rig at ECN part of TNO (formerly ECN) in Petten [18]. The model has correctly predicted the adsorption and desorption process of the CO<sub>2</sub> and H<sub>2</sub>S on hydrotalcite sorbent [50].

In this work, the model has been applied for the first time to hydrogen production using sour gases as feedstock, for which no specific experiment has been performed. However, the previous validation is considered a good reference for the predicted performance. Nevertheless, as the SEWGS performance and consumptions are not validated by specific experimental measurement, a conservative approach is performed introducing a sensitivity analysis on the SEWGS performance. The two regeneration steps (H<sub>2</sub>S released first, and then the CO<sub>2</sub>) requires the adoption of a CO<sub>2</sub> stream for the rinse step, while in CO<sub>2</sub> capture applications steam is more convenient to perform the rinse step. The purge step is carried out with low pressure steam which is generated during the cooling of the CO<sub>2</sub> and H<sub>2</sub>. The main SEWGS conditions are

reported in Table 4. In general, a techno-economic optimization should be performed to identify the best feed and purge pressure conditions: the higher the feed pressure, the higher is also the sorbent cyclic capacity with benefits for the SEWGS volume and steam consumptions. In addition, the hydrogen is produced at high pressure saving H<sub>2</sub> compression consumptions and costs. On the other side, the compression work of the syngas is higher and the rinse is more valuable with penalties in terms of efficiencies and consumptions. Two pressures were considered to see their impact on the system performance: the 21 bar was set being close to the one used in the experimental set-up in Lulea, while 16 bar is selected to assess the impact of SEWGS operating temperature (350 °C vs. 400 °C) on the process efficiency. In both cases, the compressor outlet temperature coincides with the SEWGS inlet temperature saving syngas heating/cooling with benefits on the equipment costs.

As it can be noted a wide range of operating conditions is investigated (i) to identify the optimal operating condition of the SEWGS when coupled to the AG2S (H<sub>2</sub>S recycle and temperature) and (ii) to determine the impact of the steam and rinse on the process performance.

#### Key performance indicators (KPI)

The different configurations proposed in the previous section will be compared through key performance indicators (KPI) to identify the most interesting from energy perspective. Therefore, two different indexes have been proposed. The first one (Eq. (7)) defined as hydrogen yield (H<sub>2</sub>, yield) evaluates the amount of hydrogen produced per H<sub>2</sub>S introduced into the system. The second one (Eq. (8)) aims to assess the hydrogen production efficiency ( $\eta_{H_2}$ ) and the last one (Eq. (9)) identifies the overall energy performance ( $\eta_{overall}$ ) accounting also for the steam production in the process. The three indexes are calculated as:

**Table 5 – Main assumptions for the KPI calculation.**

	Value
H <sub>2</sub> S LHV [MJ/kg]	15.201
S LHV [MJ/kg]	9.264
Electricity production efficiency	45%
HP/IP/LP production efficiency	80%/85%/90%
H <sub>2</sub> /syngas/recycle compressor efficiency	82%
Oxygen production energy	0.295 kWh/kg <sub>O2</sub>

**Table 4 – SEWGS operating conditions (\* values within brackets refers to the limits of the sensitivity analysis).**

	Case A	Case B
Operating temperature [°C]	350	400
Operating pressure [bar]	16	21
H <sub>2</sub> S–CO <sub>2</sub> separation	100%	100%
H <sub>2</sub> S recycle	98 (90-95-99.5)*	98 (90-95-99.5)*
Rinse condition		
Pressure [bar]	9.5	12.0
fluid	CO <sub>2</sub>	CO <sub>2</sub>
CO <sub>2</sub> /(CO <sub>2</sub> +H <sub>2</sub> S)	0.2 (0.1)*	0.2 (0.1)*
Purge condition		
Pressure [bar]	1.2	1.2
Steam/(CO <sub>2</sub> +H <sub>2</sub> S)	0.3 (0.2–0.5)*	0.3 (0.2–0.5)*



**Table 6 – Energy results for the base and SEWGS Cases assuming 400 °C SEWGS operating temperature.**

	Base case	SEWGS (400 °C and 21 bar)			
H <sub>2</sub> S recycle	–	90	95	98	99.5
H <sub>2</sub> S input [kg/h]	4939	4939	4939	4939	4939
H <sub>2</sub> production [kg/h]	96.2	94.4	97.4	99.2	100
H <sub>2</sub> , yield [%]	17.5	17.2	17.7	<b>18.1</b>	<b>18.2</b>
Thermal input <sub>LHV</sub> [kW]	9557	9557	9557	9557	9557
H <sub>2</sub> production [kW]	3207	3147	3247	3307	3333
HP Steam production [kW]	3016	2649	2803	2895	2940
IP Steam production [kW]	3973	4026	4306	4472	4556
LP steam consumption [kW]	17950	489	513	527	535
Syngas compressor [kW]	261	900	944	971	984
Oxygen production [kW]	553	546	538	522	496
Rinse compressor [kW]	–	79	83	85	87
<b>η<sub>H2</sub> [%]</b>	<b>10.2</b>	<b>23.3</b>	<b>23.9</b>	<b>24.2</b>	<b>24.5</b>
<b>η<sub>overall</sub> [%]</b>	<b>37.2</b>	<b>83.0</b>	<b>86.8</b>	<b>89.3</b>	<b>90.7</b>

Bold is used to outline the main numbers.

$$H_{2,yield} = \frac{mol H_2}{mol H_2S} \quad [7]$$

$$\eta_{H2} = \frac{mol H_2 \cdot LHV_{H2}}{(mol H_2S \cdot LHV_{H2S} - mol S \cdot LHV_S) + \frac{W_{el}}{\eta_{el,gen}} + \frac{Q_{th,consumed}}{\eta_{th,gen}}} \quad [8]$$

$$\eta_{overall} = \frac{mol H_2 \cdot LHV_{H2} + \frac{Q_{th,produced}}{\eta_{th,gen}}}{(mol H_2S \cdot LHV_{H2S} - mol S \cdot LHV_S) + \frac{W_{el}}{\eta_{el,gen}} + \frac{Q_{th,consumed}}{\eta_{th,gen}}} \quad [9]$$

In the  $\eta_{H2}$  and  $\eta_{overall}$ , the electric ( $W_{el}$ ) and thermal ( $Q_{th}$ ) consumptions/production are converted into primary energy through the efficiency ( $\eta$ ) of the generation processes so to have primary energy both at numerator and denominator. It is important to outline that the chemical energy input with the H<sub>2</sub>S is just the one which is actually exploited being Sulfur (S) separated and sold as by-product. The efficiency values adopted are reported in Table 5 together with the LHV of H<sub>2</sub>S and S.

Finally, it is important to account for the steam consumption/production as the processes significantly differ from this point of view.

## Results

The main results for the investigated cases are reported in Table 6 (SEWGS operating temperature and pressure of 400 °C and 21 bar) and Table 7 (SEWGS operating temperature and pressure of 350 °C and 16 bar). The adoption of SEWGS for H<sub>2</sub> separation increases the H<sub>2</sub>, yield when the recycled H<sub>2</sub>S is above 95%. The higher H<sub>2</sub>, yield is due to the possibility to push the WGS reaction inside the SEWGS towards the products (H<sub>2</sub>), thanks to the CO<sub>2</sub> absorption on the sorbent material. When H<sub>2</sub>S recycled is low, meaning that it is captured with CO<sub>2</sub>, the H<sub>2</sub>, yield is lower than the reference case which does not include CO<sub>2</sub> capture. However, the most significant advantage of the SEWGS over the base case is from the energy consumptions: the MDEA system implemented in the Base Case requires significant steam consumption for the solvent regeneration (the heat for regeneration is close to the entire H<sub>2</sub>S energy input). On the contrary, the sorbent regeneration in the SEWGS requires limited consumptions of steam (purge step, between 0.5 MW) and compression consumption for the CO<sub>2</sub> rinse (83.07 kW). About steam production, no significant differences can be

**Table 7 – Energy results for the base and SEWGS Cases assuming 350 °C SEWGS operating temperature.**

	Base case	SEWGS (350 °C and 16 bar)			
H <sub>2</sub> S recycle	–	90	95	98	99.5
H <sub>2</sub> S input [kg/h]	4939	4939	4939	4939	4939
H <sub>2</sub> production [kg/h]	96.2	94.4	97.4	99.2	100
H <sub>2</sub> , yield [%]	17.5	17.2	17.7	<b>18.1</b>	<b>18.2</b>
Thermal input <sub>LHV</sub> [kW]	9557	9557	9557	9557	9557
H <sub>2</sub> production [kW]	3207	3147	3247	3307	3333
HP Steam production [kW]	3016	2649	2803	2895	2940
IP Steam production [kW]	3973	3939	4208	4368	4449
LP steam consumption [kW]	17950	489	513	527	535
Syngas compressor [kW]	212	779	817	840	852
Oxygen production [kW]	553	546	538	522	496
H <sub>2</sub> compressor to 21 bar [kW]	–	12.9	13.3	13.5	13.6
Rinse compressor [kW]	–	69	73	75	76
<b>η<sub>H2</sub> [%]</b>	<b>10.3</b>	<b>23.8</b>	<b>24.4</b>	<b>24.8</b>	<b>25.0</b>
<b>η<sub>overall</sub> [%]</b>	<b>37.3</b>	<b>84.0</b>	<b>88.0</b>	<b>90.5</b>	<b>91.9</b>

Bold is used to outline the main numbers.

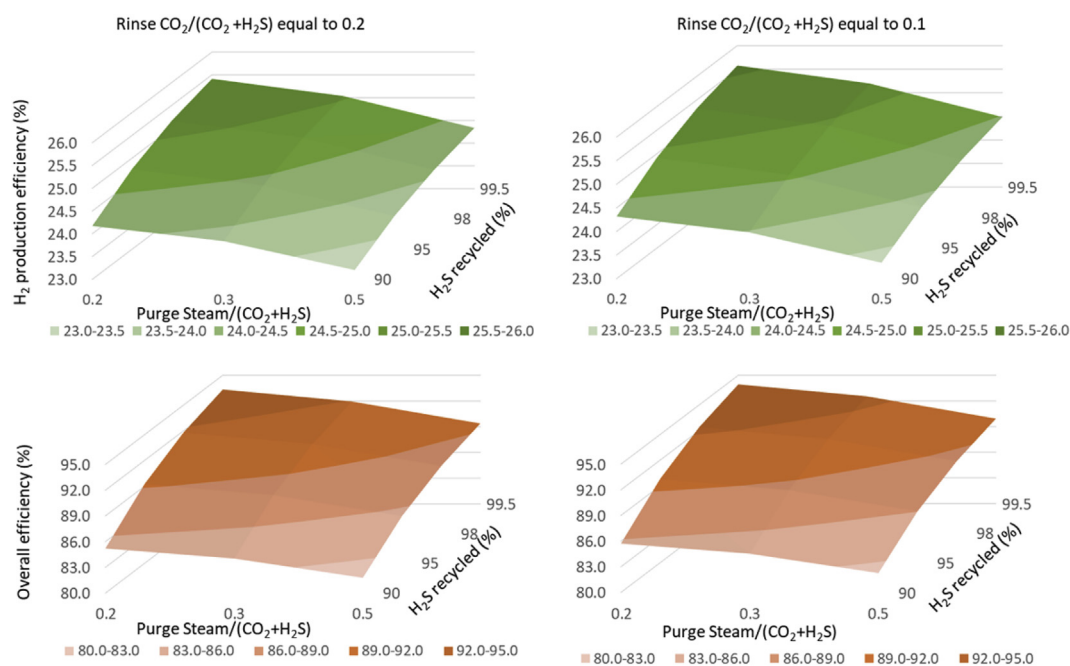


Fig. 6 –  $\eta_{H_2}$  and  $\eta_{overall}$  variation with the rinse and purge steps consumptions.

outlined between the different cases. Therefore, the  $\eta_{H_2}$  and  $\eta_{overall}$  for the SEWGS are twice the base case ones with values of 23.2–24.5% and 83.0–90.7%, respectively, at all  $H_2S$  recycles studied. Reducing the operating temperature of the SEWGS affects only the operating pressure with consequent benefits on the electric consumption as both syngas and rinse compressor have lower pressure ratio; consequently, the hydrogen production and overall efficiency increase.

Previous results outlined the potentiality of the SEWGS technology when applied to hydrogen production. The impact of the rinse and purge on the  $\eta_{H_2}$  and  $\eta_{overall}$  is reported in Fig. 6 assuming a SEWGS temperature of 350 °C; the  $H_{2,yield}$  is not affected by rinse and purge as it just depends on the recycle ratio and not the sorbent regeneration consumptions. The adoption of lower steam and  $CO_2$  flowrate for the rinse and purge steps is beneficial for both hydrogen and overall efficiency though with very limited variations. In particular the  $H_2$  production efficiency ranges from 26.0% of the most optimistic case (Rinse 0.1, purge 0.2,  $H_2S$  recycle 99.5%) down to 23.3% for the worst case (Rinse 0.2, purge 0.5,  $H_2S$  recycle 99.5%). A higher impact can be noted on the overall efficiency in absolute value (from 94% to 82.5% of the same cases above), but in relative terms it is similar to the one before and equal to 12%. The efficiency is only slightly affected by steam consumptions as the heat duty for steam production is quite low with respect to other terms as steam production (see Tables 6 and 7) also because cycle is designed to recover most of the latent heat from the steam condensation, minimizing the impact of rinse and purge steam demand. The case at 400 °C has similar trend, so it is not reported for sake of brevity.

In general, the sensitivity analysis confirms the interest in applying SEWGS for  $H_2$  separation even assuming higher consumptions. The benefit of simultaneous  $H_2S/CO_2/H_2$

separation at high temperature are more relevant than the specific consumptions for the regeneration.

## Conclusions and outlooks

This paper discusses the potentiality of Sorption Enhanced Water Gas Shift (SEWGS) application to the  $H_2$  production process called AG2S™ which uses  $H_2S$  and  $CO_2$  as feedstock. In the AG2S™, the  $H_2S$  reacts at 1000 °C with the  $CO_2$  producing  $H_2$  and elemental sulfur together with other by-products as CO and water. Usually  $H_2$  purification is carried out at low temperature with amine scrubbing, which is energy intensive and absorbs both the unreacted  $H_2S$  and  $CO_2$ . Benefits of SEWGS integration are (i) low regeneration energy, (ii)  $H_2S$  and  $CO_2$  can be separated during the regeneration step so that  $H_2S$  can be recycled and  $CO_2$  captured, (iii) the  $H_2S$  and  $CO_2$  adsorption pushes the  $H_2O$  and CO conversion to even more  $H_2$ , boosting the efficiency. Detailed mass and energy balances showed that  $H_2$  production efficiency, which accounts as process output only the  $H_2$ , moves from 10% of the amine scrubbing case to the 25.0% of the SEWGS case. Considering a more general efficiency index, where the steam production is also accounted, the SEWGS lay-out outperforms the MEA case by 50% points (90% vs 38%). In addition, a sensitivity analysis on the SEWGS outlined the benefits of this concept in a wide range of performance. Future works will focus on a case study to assess the economic benefits of the proposed technology vs. the conventional one and commercially available technologies for  $H_2$  production. In this future study, a system optimization will be carried out optimizing the SEWGS operating conditions. Finally, test campaign of the SEWGS performance under these operating conditions will be performed at the lab-

scale conditions in Petten to confirm the performance assumed in this work.

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