Research Article

# On the Effect of the Reaction Medium on the HydroClaus Process: A Novel Sustainable H$_2$S Valorization Strategy

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**ABSTRACT:** Hydrogen sulfide (H$_2$S) is becoming a critical issue to manage, due to the increasing sulfur content in the processed gas together with the stricter environmental regulations. Novel alternatives are being developed for the H$_2$S abatement and conversion to valuable chemicals. Among them, the HydroClaus process, patented by Eni S.p.A., deserves attention. This technology aims at converting H$_2$S and SO$_2$ into a hydrophilic mixture of sulfur and sulfur-rich compounds, polythionates, to be used as a fertilizer. An improved configuration for an efficient water management is proposed in this work. The process operability has been demonstrated at the bench scale, through an ad hoc experimental campaign. For the technology scale-up, a flowsheet has been set up and its performances have been assessed in terms of heat and material balances and CO$_2$ emissions. Results reveal that the modified HydroClaus process can be a valid solution for an effective H$_2$S valorization, also considering that no direct CO$_2$ emissions are released. Moreover, since only electric power is required, a further reduction of the indirect CO$_2$ emissions is expected, if renewable sources can be exploited for this purpose.

**KEYWORDS:** H$_2$S valorization, green process, CO$_2$ emissions reduction, waste-to-valuable chemicals, water saving
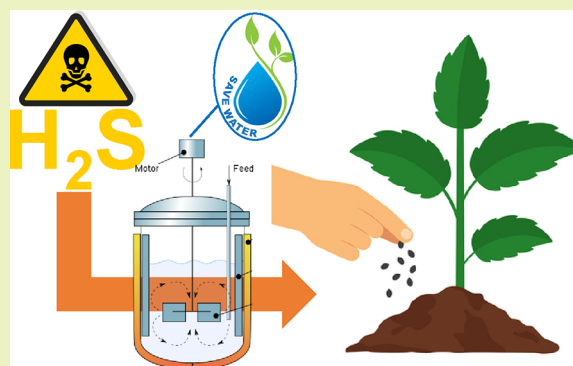
## ■ INTRODUCTION

Hydrogen sulfide (H$_2$S) is a colorless, flammable, highly toxic gas, frequently found in the oil and gas or pulp and paper industries.[1] Due to its effects on the environment and human body, it needs to be captured and converted.[2] Several processes have been developed to accomplish gas purification from H$_2$S, considering simple once-through operations or complex multiple-step systems.[3] Nowadays, the most widespread technique for gas purification from H$_2$S is the acid gas chemical absorption with amines and its subsequent conversion to elemental sulfur in the Claus unit.[4] The Claus process is particularly suitable for both large-scale sulfur production and high H$_2$S concentration in the feed gas. On the other hand, for relatively small flow rates, liquid H$_2$S reduction−oxidation (redox) processes are quite common. In this case, H$_2$S is absorbed from a gas stream through contact with a redox solution and directly converted to sulfur, in the form of an aqueous slurry. Some of the most diffused liquid H$_2$S redox processes are THIOPAQ (Paqell), CrystaSulf (AECOM), and LOCAT (Merichem).

Because of the increasing sulfur content in natural gas,[5−7] the key player fuel of the energy transition era, and the stricter environmental regulations, managing the rising H$_2$S level is becoming a challenge. For this reason, research efforts are devoted to developing novel H$_2$S utilization[8,9] and valorization

technologies as an alternative to the conventional treatments.[10,11] These technologies are highly attractive because they allow the simultaneous H$_2$S abatement and the production of high value-added chemicals. When H$_2$S is converted, two different kinds of products can be obtained: H$_2$-based and sulfur-based. The H$_2$ production from H$_2$S is getting attention. Nevertheless, at the moment, the Technology Readiness Level (TRL) of these processes is too low for the scale-up to the industrial stage.[7,12,13] On the other hand, H$_2$S to sulfur and sulfur-based compounds is a much more consolidate strategy. In this panorama, Eni S.p.A. proposed a novel H$_2$S oxidation technology, the proprietary HydroClaus process, dedicated to the production of a high value-added colloidal sulfur.[14,15] The HydroClaus process consists in the liquid phase oxidation of H$_2$S by SO$_2$ (reactions 1, in the past known as Wackenroder reaction,[16] and 2), thus performing essentially complete H$_2$S removal and conversion into sulfur and polythionates. The
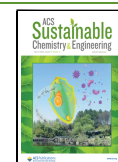
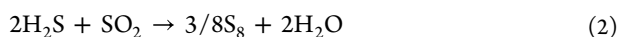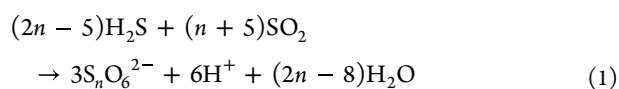reaction product, a sulfur and polythionate mixture, can be used as fertilizer and soil improver for agriculture, also where the very alkaline soil pH hinders the cultivation.[17] These kinds of sulfur-based fertilizers are effective in lowering the pH of the soil, despite alkaline soils being usually difficult to correct. Moreover, the combined effect of sulfur and polythionates is helpful in providing plant nutrients in both short and long terms. Together with agriculture, polythionates can find application in several more specific fields, as in the chemical milling of magnesium and its alloys, in the metal machining or in gold leaching processes.
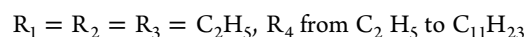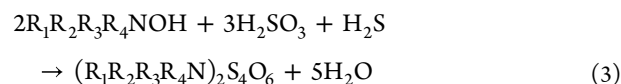
The typical process operating conditions are ambient pressure, ambient temperature, and acidic pH from 3 to 2. The inlet reactant ratio determines the type and distribution of products: sulfur and short-chain polythionates are preferentially produced if an excess of $H_2S$ is fed, while $S_nO_6^{2-}$, with $n$ ranging from 4 to 8, is the main product when $SO_2$ is the most abundant reactant.[17] Together with the reactant ratio, also the pH of the reaction environment affects the nature of the products: with increasing pH, the amount of produced sulfur is lower and polythionates become shorter up to the formation of thiosulfate only, at pH > 8.[18]

$$(2n - 5)H_2S + (n + 5)SO_2$$
$$\rightarrow 3S_nO_6^{2-} + 6H^+ + (2n - 8)H_2O \qquad (1)$$

$$2H_2S + SO_2 \rightarrow 3/8S_8 + 2H_2O \qquad (2)$$

For the HydroClaus process demonstration and in view of its industrialization, an extensive experimental campaign has been performed at the bench scale. The optimal reaction conditions were proved to be high residence time and low temperature, to enhance the stability of the colloid produced. The collected experimental data have been modeled through a suitable kinetic scheme, to favor the technology scale-up.[19] Also, the experimental campaign confirmed the $CO_2$ tolerance of the process, since carbon dioxide is inert in the reaction zone. Depending on the acid gas feed composition and the sweetening technology implemented upstream the sulfur recovery section, the optimal $CO_2$ content can be selected to minimize the HydroClaus energy requirements. Having finalized the experimental stage, a process techno-economic assessment has been performed to identify the technology cost drivers and eventually manage them. This analysis revealed that a proper handling of the process water can possibly lower the process operating costs, thus leading to higher revenues. In its traditional configuration, water is the reaction medium in the HydroClaus technology: polythionates are produced in water as hydrophilic sulfur colloid. At a first glance, some efforts were made to scan the possible alternatives for the water separation from the polythionate mixture. Nevertheless, this issue was quite challenging, since polythionates are extremely thermolabile; thus, all the separation techniques involving heating (as distillation or evaporation) have to be avoided. Also, ad hoc special formulized membranes have been tested but turned out to be not applicable because of consistent fouling issues. Due to the not easy water separation downstream the reaction section, the physical−chemical features of the reacting system were investigated to identify the possible alternatives to water for the reaction medium. The ideal reaction medium has not to interfere with the HydroClaus kinetics, rather promoting the polythionate formation, allowing the spontaneous water−polythionate separation. In this work, the effect of the reaction medium on the HydroClaus technology is presented. After a massive literature search and a preliminary experimental campaign, amine-based species have been selected as the most promising candidates. Having proved the satisfactory organic-aqueous phase separation and the feasibility of the reaction at the bench scale, a process scheme has been set up for the technology scale-up to the industrial level, whose performances have been analyzed in terms of heat and material balances and $CO_2$ emissions. Results show that no direct $CO_2$ emissions are released. Moreover, since only electric power is required, a further reduction of the indirect $CO_2$ emissions is expected, if renewable sources can be exploited for the purpose. In conclusion, the HydroClaus technology turns out to be a sustainable waste to valuable chemical alternatives, following the circular economy concepts.

**Reaction Medium Selection.** The best candidate to replace water as reaction medium has to favor the spontaneous polythionate liquid−liquid separation. The most common species only slightly soluble in water to promote such a separation are the organic-based species (see Table 1). However, only few of them show physical−chemical features compatible with the process chemistry. Also, polythionates are not so common and not so widely studied in the available literature. After a widespread literature search, the amine-based HydroClaus process has been introduced as a possible solution, leading to the production of organic-based polythionates. In this case, polythionate formation occurs through the reaction exemplified in 3 for tetrathionate, which is instantaneous at ambient temperature. Depending on the ammonium choice, the reaction product, that is, the polythionate of the organic base, may be a viscous oil, not soluble in water, which separates spontaneously from the aqueous phase as an additional liquid phase,[20] thus favoring the water recovery.

$$2R_1R_2R_3R_4NOH + 3H_2SO_3 + H_2S$$
$$\rightarrow (R_1R_2R_3R_4N)_2S_4O_6 + 5H_2O \qquad (3)$$

$$R_1 = R_2 = R_3 = C_2H_5, R_4 \text{ from } C_2H_5 \text{ to } C_{11}H_{23}$$

Literature related to polythionate formation in the organic phase is outdated and thus lacks modern chemical characterization techniques. Different experimental methods have been tested,[21] and several organic compounds have been analyzed as catalysts for the polythionate production.[22] The main literature experimental tests performed, as well as the used organic bases, are summarized in Table 1.

In addition to those reported in Table 1, the thiosulfuric acid decomposition has been analyzed in the presence of salts of diethyldecyl-, diethyldodecyl-, tributyl-, triisoamyl-, trihexyl-, triheptyl-, tri-$n$-decyl-, octadecyl-, methyloctadecyl-, and diethyl-$\beta$-phenoxyethylamine as well as salts of trimethyldecyl-, dimethylisoamyldecyl-, dimethylisoamyldodecyl-, and dimethylisoamylbenzyl ammonium.[22]

The following achievements are reported in the literature.

(1) Primary amines ($RNH_3^+$) do not favor the formation of polythionates. Ammonia can be interpreted as a degeneration of the primary amine (unsubstituted nitrogen) and thus has no catalyzing effect on the Wackenroder reaction.[21]

(2) Secondary amines ($R_2NH_2^+$) with a sufficiently long hydrocarbon substituent favor the tetrathionate formation.[21]

(3) Tertiary amines with an alkyl substituent containing more than five carbon atoms favor the tetrathionate formation,

**Table 1. Experimental Methods Available in the Literature for the Production of Organic Bases, Together with the Corresponding Literature Reference**

| reactants | organic species | formula | reference |
|---|---|---|---|
| $Na_2S_2O_3$ + HCl in $H_2O$ | N,N-diethylnonylamine, trioctylamine | $C_{13}H_{29}N$, $C_{24}H_{51}N$ | 21 |
| $SO_2$ + $H_2S$ in EtOH | N,N-diethylnonylamine, trioctylamine | $C_{13}H_{29}N$, $C_{24}H_{51}N$ | 21 |
| $Na_2S_2O_3$ + HCl in $H_2O$ | N,N-diethylnonylamine, trioctylamine | $C_{13}H_{29}N$, $C_{24}H_{51}N$ | 21 |
| $SO_2$ + $H_2S$ in EtOH | alkyltriethylammonium hydroxide | $R(C_2H_5)_3NOH$, with R containing 2 to 11 carbon atoms | 23 |
| $Na_2S_2O_3$ + HCl in EtOH | 8-alkoxyquinoline, N-methyl-8-alkoxyquinoline | $C_{14}H_{34}NO$, $C_{15}H_{19}NO$, $C_{16}H_{21}NO$, $C_{18}H_{25}NO$, $C_{16}H_{21}NO$ | 24 |
| $Na_2S_2O_3$ + HCl in EtOH | N-2-butoxyethyldiisopentylamine, N-2-(pentyloxy)ethyldiisopentylamine, N-2-(isopentyloxy)ethyldiisopentylamine, N-2-(hexyloxy)ethyldiisopentylamine, N-2-(heptyloxy)ethyldiisopentylamine, N-2-(octyloxy)ethyldiisopentylamine, N-2-(nonyloxy)ethyldiisopentylamine, triisopentylamine | (iso-$C_5H_{11}$)$_2$NCH$_2$CH$_2$OR, with R containing four to nine carbon atoms | 25 |

while amines containing two or three long hydrocarbon chains favor the pentathionate formation, with a yield that increases as the chain length increases.[21,23]

(4) Quaternary ammonium bases, with a sufficiently long chain, favor the formation of tetrathionates mainly and, to a lower extent, of pentathionates.[25]

(5) Factors such as the presence of heteroatoms (oxygen) in the amine substituents, the strength of the organic base, and its solubility in dilute acids have no influence on the catalytic activity.[25]

To verify the effectiveness of an organic base in solving the problem of the water management in the HydroClaus process, the experimental analyses presented in the next section were set up.

**Experimental Investigation: Synthesis of Decylpyridinium Polythionates ($C_{10}Py$ Polythionates).** The effect of the reaction medium on the HydroClaus process has been proved through an ad hoc experimental campaign. Tests with a decylpyridinium hydroxide were performed to highlight its effect on the polythionate formation. The target decylpyridinium polythionate was first prepared, characterized through NMR and FTIR analyses, and its thermal stability over time and water solubility was assessed.

Decylpyridinium polythionate ($C_{10}Py$ polythionate) was synthetized and characterized to evaluate the physical state, thermal stability, and water solubility. ($C_{10}Py$ polythionate) was prepared using the optimized method reported by Volynskii and Smolyaninov (4) starting with decylpyridinium chloride ($C_{10}PyCl$) and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$).
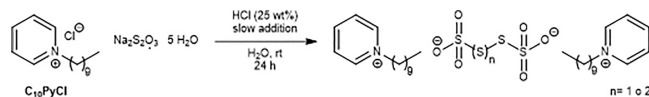


1.327 g of $Na_2S_2O_3 \cdot 5H_2O$ (1.5 eq) previously dissolved in 10 mL of $H_2O$ was added to a solution prepared by dissolving 0.912 g of $C_{10}PyCl$ (1.0 eq) in 7 mL of $H_2O$. Then, 2 mL of HCl (10 wt %) was slowly added (over 8 h) to the resulting solution. A high addition rate of the acid solution involves the formation of elemental sulfur and subsequent reduction of the desired product. After the first few additions, the solution turned to deep yellow color and then a milky suspension was obtained. The suspension was left under gentle agitation for 16 h. At the end, 10 mL of dichloromethane was added and the organic phase was separated from the aqueous phase, anhydrified with magnesium sulfate, filtered, and dried at reduced pressure. The resulting crude mixture was dissolved in methanol, and the precipitated sulfur was removed by filtration. The solvent was evaporated under reduced pressure at 60 °C for 6 h.

The obtained product appears as a dark-yellow viscous oil with an overall yield of 61.5 mol %. The structure was confirmed by $^1H$- and $^{13}C$-NMR and FTIR, and the spectra are shown in Figures 1 and 2, respectively. On the basis of chemical structure and physical state, it is possible to classify $C_{10}Pyr$ polythionate as room-temperature ionic liquid (RTIL).

In addition, the thermal stability as a function of time of the $C_{10}Py$ polythionate was evaluated by heating the compound at 120 °C for 24 h. For this purpose, the FTIR spectrum of the starting compound was compared with that at the end of treatment (Figure 2). Based on the data, $C_{10}Py$ polythionate appears to be stable at 120 °C for a long time since no structural modifications were observed from the comparison.
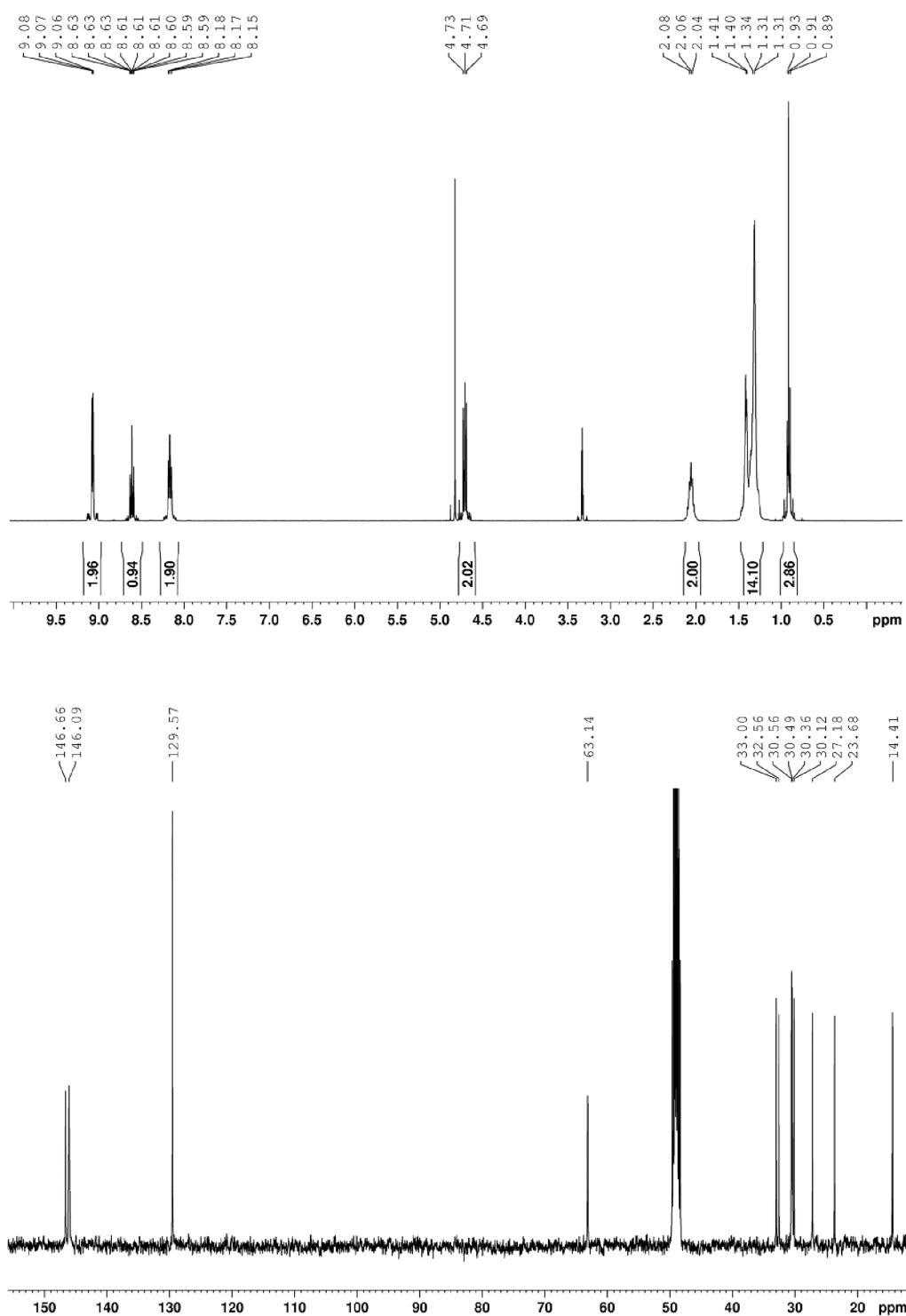
**Figure 1.** $^1$H- and $^{13}$C-NMR of decylpyridinium polythionate.

The water solubility of $C_{10}$Py polythionate was assessed by adding consecutive amounts of water to 100 mg of sample until complete dissolution. The tests were repeated in triplicate, and the solubility in water was <1 wt %. $C_{10}$Py polythionate forms a milky suspension in water that can be separated by simple centrifugation.

The explorative experimental campaign satisfactorily confirmed the amine-based HydroClaus process at the bench scale. According to reaction 3, two different phases were produced: the heavy one, a yellowish viscous oil, in which polythionates are concentrated, and the light one, which is the aqueous phase, essentially free of sulfur in the process, thus minimizing water requirements and wastes.

**Process Scheme Assessment.** Due to the encouraging results of the experimental campaign, a preliminary process scheme has been set up for the industrialization of the amine-based HydroClaus process.

The proposed flowsheet, as simulated in Aspen Plus V11, is reported in Figure 3. An existing Eni S.p.A. Claus plant has been selected as a reference for defining the inlet stream conditions
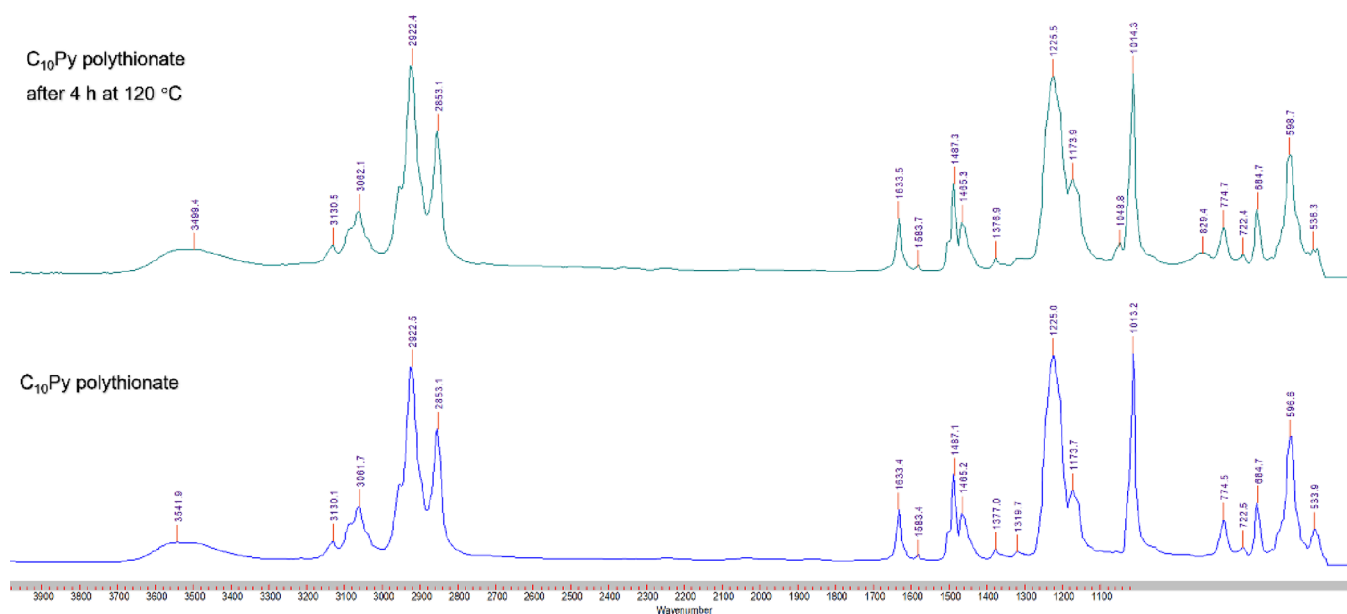
**Figure 2.** FTIR of decylpyridinium polythionate before (blue line) and after (green line) the treatment at 120 °C for 24 h.
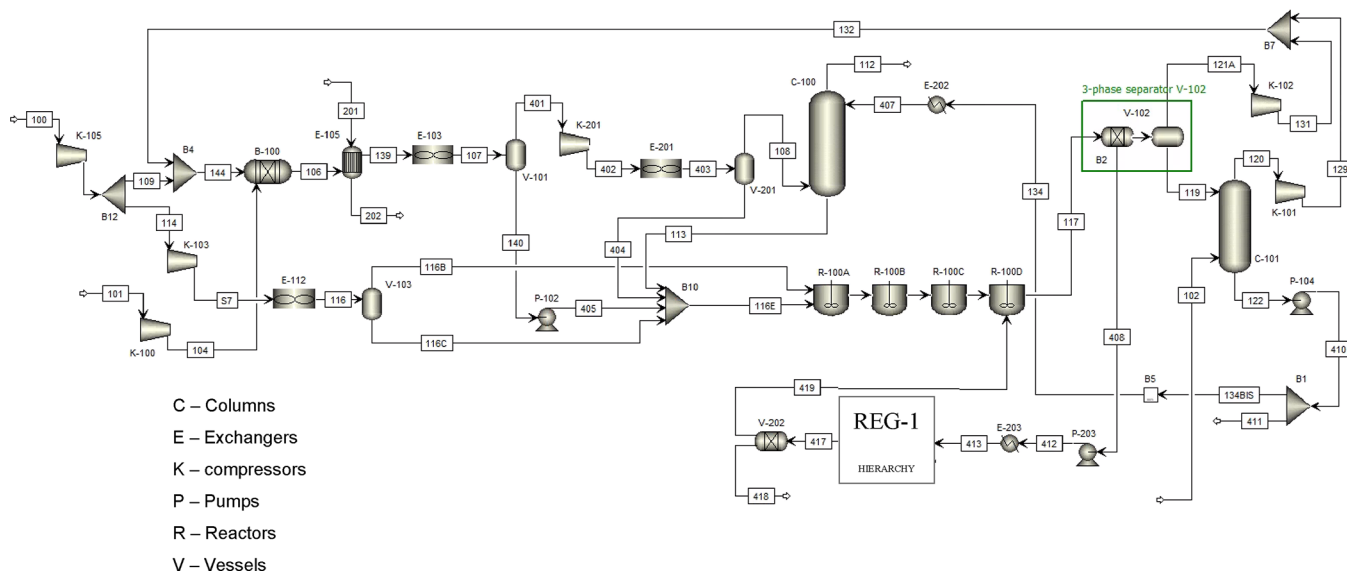


**Figure 3.** Process scheme for the organic base polythionates production. Simulation in Aspen Plus V11.

**Table 2. Inlet and Outlet Stream Specifications at the Process Unit Battery Limits for the Amine-Based HydroClaus Process of Figure 3**

| | | inlet streams | | | outlet streams | |
|---|---|---|---|---|---|---|
| stream | | 100 | 101 | 102 | 112 | 418 |
| T | °C | 44.3 | 30 | 30 | 28.8 | 40 |
| P | bara | 1.8 | 1 | 1.1 | 7.9 | 3.5 |
| Molar fractions | | | | | | |
| $H_2S$ | | 0.7038 | | | | |
| $CO_2$ | | 0.2440 | | | 0.0735 | |
| $SO_2$ | | | | | 0.0007 | |
| $H_2O$ | | 0.0522 | | | 0.0056 | |
| $S_8$ | | | | | | 0.0015 |
| $O_2$ | | | 0.21 | 0.21 | 0.0050 | |
| $N_2$ | | | 0.79 | 0.79 | 0.9152 | |
| $K_2S_4O_6$ | | | | | | 0.9985 |
| $F_{TOT}$ | kmol/h | 116.9474 | 370.0000 | 80.0000 | 388.4245 | 18.4599 |

for the process simulation. Also, this allowed an immediate comparison of the proposed technology with the traditional Claus one.

Elect-NRTL was selected as the property package to represent the system's thermodynamic behavior.

The process is fed with an acid gas stream (100 in Figure 3), whose specifications are provided in Table 2, together with air (101 in Figure 3). The overall sulfur productivity (almost completely in the form of the polythionates) is fixed at 63.0 tpd. The process scheme can be distinguished into different subsections, each described in the following.

(1) Combustion section. In this section, a portion of the $H_2S$ fed to the unit battery limits is converted to $SO_2$ by oxidation with air in the furnace B-100, simulated through the R-Gibbs module of Aspen Plus. The air flow rate entering the process is selected to guarantee the quantitative $H_2S$ oxidation to $SO_2$. At the furnace outlet, the high enthalpy content associated with the outlet stream is recovered producing high-pressure steam into the E-105 waste heat boiler.

(2) Absorption section. The absorption section is essentially composed of the absorption tower C-100, in which the $SO_2$-rich gas, 108 in Figure 3, compressed up to 8 bar in K-201, is absorbed with water (stream 407), entering the tower at 30 °C. The process water is selected to ensure that the outlet liquid has a $SO_2$ maximum content of 6.2 wt %, which is the acceptable threshold concentration before severe corrosion issues occur.

(3) Reaction section. The reaction section is fed with the $H_2S$-rich stream, the liquid phase $SO_2$ stream coming from the previous absorption unit, and the amine regenerated in the amine regeneration section. The ammonium hydroxide selected for process simulation was decylpyridinium hydroxide ($C_{15}H_{27}NO$), which fulfills the catalytic species requirements reported in the previous section. Its flowrate is chosen to comply with the stoichiometry of reaction 3, as well as the ones of $H_2S$ and $SO_2$ entering the reaction zone, which consists of a four-CSTR series. The kinetic model implemented in this section has been derived in our previous work.[19] While the $H_2S$ gas and the $SO_2$-saturated liquid streams are fed to the first CSTR, the ammonium hydroxide from the regeneration section is fed to the last one, where most of $S_4O_6^{2-}$ has already been produced. In this way, reaction 3 can take place with a higher $C_{10}Py$ polythionate conversion. The outlet mixture, that is, a gas–liquid–liquid mixture, is sent to a three-phase separator (V-102). Here, the gas phase (121A in Figure 3), essentially containing unreacted $H_2S$ and $SO_2$, is recycled back to the combustion section. The aqueous phase (119 in Figure 3) is purified by air stripping in the C-101 column. The dissolved gas is recycled back, while the liquid phase, an almost pure water stream, is returned to the absorption tower C-100. The organic phase, in which polythionates are present together with the organic base, is purified in the amine regeneration section.

(4) Amine regeneration section. This section allows, through a system of ion exchange resin beds (REG-1), the regeneration of ammonium hydroxide and the production of polythionate salts (mostly potassium polythionates). The ammonium hydroxide is recycled back to the reaction section (419 in Figure 3), thus realizing a closed loop,

while the polythionate product can be stored to be commercialized (418 in Figure 3).

## ■ RESULTS AND DISCUSSION

**Heat and Material Balances.** The amine-based Hydro-Claus process requires no valuable chemicals: in addition to the acid gas stream, air and water are fed to the process unit battery limits, only. Air is necessary for the $H_2S$ combustion and the aqueous phase stripping, while water is needed to absorb the gaseous phase $SO_2$. The ammonium hydroxide required for the reaction to occur is regenerated downstream of the reaction section, by means of ion exchange resin beds. Table 2 shows the inlet and outlet stream specifications at the process unit battery limits. The overall sulfur recovery is equal to 99.7%, which meets the highest standards of the state-of the-art SRU processes. The few sulfur losses correspond to the amount of $SO_2$ in the recycle water, which is not polished, and, if a recovery >99.99% is needed, this is easily achievable considering the addition of a water post-treating section or a deeper $SO_2$ stripping in the C-101 column. The off-gas leaving the absorber is quite clean since it contains practically no $H_2S$ and only 660 ppmv of $SO_2$, meaning that it can be simply vented without incineration. The outlet temperature of the burner B-100 is equal to 1645 °C, which is slightly higher than the refractory preservation threshold. However, this issue can be easily solved with an advanced burner design solution, typical of some commercial alternatives (as in the COPE process, licensed by Fluor, in which part of the cool gases is recycled back to the furnace). A significant production of high-pressure steam is observed downstream of the burner, which is an additional advantage of the present technology. The per-pass conversion of the two reactants is equal to 79.2% both for $H_2S$ and $SO_2$. This is consistent with the experimental observations, according to which a $H_2S$ conversion between 75 and 90% is achieved. The reaction product leaving the series of CSTRs has a temperature of 52.1 °C, at which no degradation should occur due to enhanced stability of the amine−polythionate complex compared to the polythionic acid one.

The energy requirements of the amine-based HydroClaus process are summarized in Table 3, considering the heating and

**Table 3. Heating and Cooling Requirements of the Amine-Based HydroClaus Process Illustrated in Figure 3**

| unit | duty [kW] | $T_{in}$ [°C] | $T_{out}$ [°C] | utility |
|------|-----------|---------------|----------------|---------|
| E-105 | 8273 | 1645.4 | 255.4 | boiler feed water (BFW) |
| E-103 | 1662 | 255.4 | 50 | air |
| E-112 | 31.0 | 114.1 | 50 | air |
| E-201 | 1005 | 215 | 50 | air |
| E-202 | 1682 | 49.1 | 29.7 | cooling water (CW) |
| E-203 | 63.2 | 52.3 | 40 | cooling water (CW) |

cooling duties, and in Table 4, considering the electric power consumptions. As can be observed, no significant heating and cooling requirements are requested. The working fluid selected at the utility side is cooling water or air in all cases. Only electric energy consumption results to be not negligible in the process energy balance.

**$CO_2$ Emissions.** To further assess the process performances and verify the sustainability of $CO_2$, its equivalent emissions have been evaluated. The equivalent $CO_2$ emission analysis is a modern tool that has emerged because of the increasing interest in the evaluation of the greenhouse gas (GHG) emissions of an

**Table 4. Power Requirements of the Amine-Based HydroClaus Process Illustrated in Figure 3**

| unit | $P_{in}$ [bara] | $P_{out}$ [bara] | power [kW] |
|------|------|------|------|
| K-100 | 1.8 | 3.5 | 356.8 |
| K-101 | 1 | 3.5 | 109.9 |
| K-102 | 1.2 | 2.5 | 15.2 |
| K-103 | 2.5 | 3.6 | 14.6 |
| K-105 | 1.8 | 2.5 | 38.1 |
| K-201 | 2.1 | 8 | 772.0 |
| P-102 | 2.1 | 3.5 | 0.05 |
| P-104 | 1 | 8.2 | 22.0 |
| P-203 | 1.5 | 5 | 1.7 |

industrial plant.[26] Among the most widespread methods in the European industry, the European Investment Bank Project Carbon Footprint Methodologies[27] have been applied in this work, according to which the process emissions are classified into three different categories:

(1) Direct GHG emissions, which physically occur from sources that are operated by the project, for example, emissions produced by the combustion of fossil fuels, by industrial processes, and by fugitive emissions, such as refrigerants or methane leakage.

(2) Indirect GHG emissions, associated with energy consumption such as electricity, heating, cooling, and steam.

(3) Other indirect GHG emissions that can be considered a consequence of the activities related to the production (e.g., emissions related to the extraction of raw material or feedstock and vehicle emissions from the use of road infrastructure, including emissions from the electricity consumption of trains and electric vehicles).

Based on this methodology, the following hypotheses have been introduced for the evaluation of the amine-based HydroClaus process $CO_2$ emissions:

(1) the only gas released into the atmosphere with a significant global warming potential (GWP) is $CO_2$. The contributions of the other gases are neglected. For direct $CO_2$ emission evaluation, 8000 working hours per year are assumed;

(2) concerning the indirect $CO_2$ emissions, those associated with electricity consumption (eq 5), cooling requirements (eq 6), and steam production or consumption (eq 7) are accounted for. For electric consumption, 445.5 $g_{CO_2}$/kWh is assumed, as reported in the ISPRA report,[28] while for the cooling water circuit the Turton method is considered, introducing a conversion factor ($f$ in eq 6) between electric and thermal energies that depends on the inlet and outlet water temperature[29] (from 45 to 75 °C $f$ = 0.00477; from 25 to 45 °C $f$ = 0.00715; from 25 to 35 °C $f$ = 0.01431);

(3) the fugitive emissions and the other indirect GHG emissions (category 3) are neglected.

$$\dot{m}_{CO_2}\left[\frac{t_{CO_2}}{y}\right] = \dot{W}_{el}[kW] \cdot 8000\left[\frac{h}{y}\right] \cdot 445.5\left[\frac{g_{CO_2}}{kWh}\right] \cdot$$
$$\frac{1}{10^6}\left[\frac{t_{CO_2}}{g_{CO_2}}\right] \tag{5}$$

$$\dot{m}_{CO_2}\left[\frac{t_{CO_2}}{y}\right] = Q[kW_t] \cdot f\left[\frac{kW_e}{kW_t}\right] \cdot 445.5\left[\frac{g_{CO_2}}{kWh_e}\right] \cdot$$
$$8000\left[\frac{h}{y}\right] \cdot \frac{1}{10^6}\left[\frac{t_{CO_2}}{g_{CO_2}}\right] \tag{6}$$

$$\dot{m}_{CO_2}\left[\frac{t_{CO_2}}{y}\right] = Q\left[\frac{kJ_t}{h}\right] \cdot \frac{1}{\eta}\left[\frac{kJ_{comb}}{kJ_t}\right] \cdot LHV\left[\frac{t_{fuel\ gas}}{kJ_{comb}}\right] \cdot$$
$$2.75\left[\frac{t_{CO_2}}{t_{fuel\ gas}}\right] \cdot 8000\left[\frac{h}{y}\right] \tag{7}$$

Results for the $CO_2$ emission evaluation are reported in Figure 4. As can be observed, the amine-based HydroClaus process shows negative net equivalent $CO_2$ emissions. This means that, even if the process releases some $CO_2$ to the atmosphere, namely, that entering the process together with the acid gas stream, the steam produced in the $CO_2$-free waste heat boiler
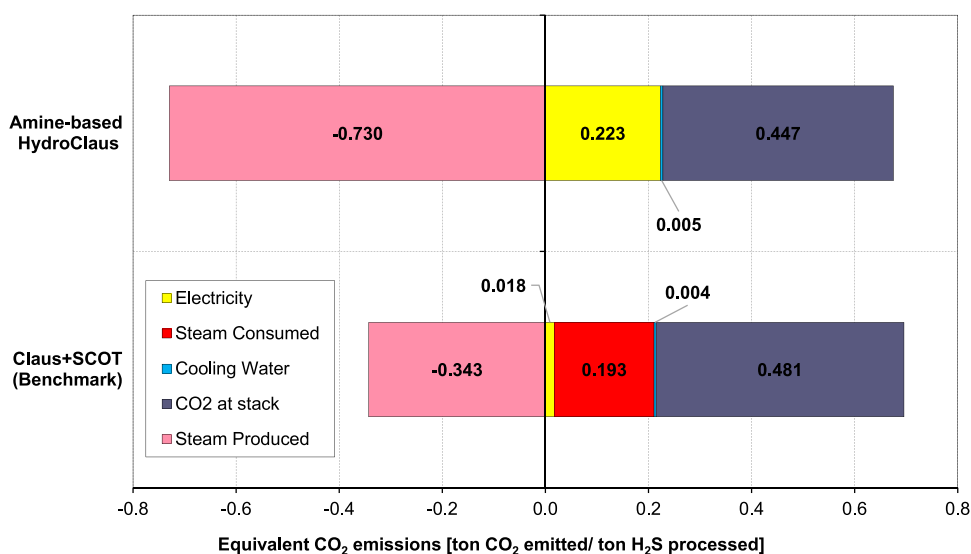


**Figure 4.** Equivalent $CO_2$ emissions for the amine-based HydroClaus process, considering the partition between the different contributions.

compensates this contribution. For this reason, the amine-based HydroClaus process can be considered as a carbon-negative process in the wider plant context. Moreover, the process is totally based on electric power requirement and, due to the increasing penetration of the renewable energies, a further reduction of the equivalent $CO_2$ emissions is expected. Also, the comparison with the benchmark Claus + SCOT process reveals that the amine-based HydroClaus is competitive with respect to the traditional sulfur recovery process.

## CONCLUSIONS

In this work, a novel alternative for the $H_2S$ valorization is presented, that is, the HydroClaus process, patented by Eni S.p.A., for the $H_2S$ conversion into a hydrophilic mixture of sulfur and sulfur-rich compounds, the polythionates. The reaction product is an environmentally friendly soil conditioner, increasing rapidly the pH value of alkaline soils and making them cultivable for different plant species. These novel soil conditioners have been formulated to provide plant essential nutrients, allowing water-saving and being environmentally friendly at the same time.[30] Nevertheless, due to the high polythionate versatility, the produced sulfur mixture can find applications in different fields (i.e., in solutions for chemical milling of magnesium and its alloys; lubricants—coolants for metal machining; eluting agents in gold leaching processes).[22]

Specifically, an improved HydroClaus configuration is discussed, for a simpler process water management. To solve this issue, amines have been introduced in the reaction section, leading to the production of organic-based polythionates. The selected $C_{10}Py$ polythionate has been synthetized by an optimized synthetic procedure and has been characterized by NMR and FTIR. Furthermore, its thermal stability and water solubility have been evaluated. Polythionic acid slurries obtained through the amine-mediated HydroClaus process seem to be promising, but some features of this process have to be verified such as polythionic acid stability during the time and polythionic acid stability in the presence of metal surfaces, which can promote polythionic acid decomposition to sulfur and $SO_2$. An explorative experimental campaign has been further performed at the bench scale, to verify the effective water—product separation. A process scheme has been set up to achieve a preliminary evaluation of this new process. Its performances are discussed considering the heat and material balances and related $CO_2$ emissions. From this preliminary evaluation, the process totally relies on electric power and it can be carbon negative.

Future work in this respect will regard the deepening of product stability, the analysis of the amine solution regeneration, and an in-depth experimental campaign, for the complete assessment of the reacting system behavior.

If the calculated performances of the amine-based Hydro-Claus process will be confirmed by experimental data settings, the amine-mediated HydroClaus process can be considered an interesting alternative to middle scale processes for $H_2S$ removal and conversion.

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### Notes

The authors declare no competing financial interest.

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