Simulation And Sustainability Assessment Of H₂S Utilization From Acid Gas On Haldor Topsoe Wet Gas Sulfuric Acid And Claus Processes

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ABSTRACT: Claus process is a widely adopted process to reduce emissions from refineries by converting H₂S into elemental sulfur. On the other hand, Haldor Topsoe's Wet Gas Sulfuric Acid (WSA) is an alternative to convert H₂S directly into sulfuric acid. The purpose of this project was to simulate both of these state-of-the-art technologies and evaluate their suitability for various acid gas capacity and H₂S concentrations. Three sustainability pillars of people (safety), planet (environment), and profit were used as the comparison metrics. The developed simulation (1st principle) models were used to generate lots of data as the basis for subsequent development of regression models. The latter models were used in the comparisons for they are much faster in calculations than the 1st principle models. The results showed that the WSA process was safer (lower Fire and Explosion Damage Index), more environmentally friendly (lower Global Warming Potential), and more profitable (higher annual profit) in most of the evaluated operating conditions.

Key words: Acid Gas Removal, H₂S Conversion, Wet Gas Sulfuric Acid, Sustainability, Regression Analysis

1. INTRODUCTION

H₂S is a typical contaminant found in crude natural gas, extracted from the oil and gas wells and refineries. Its amount in natural gas varies significantly from wells to wells. It is a colourless, flammable and poisonous gas. It has a molecular mass of 38 g/mol with boiling point at -60.3 °C. The mixture of H₂S and air is explosive. It is a very corrosive gas which can cause corrosion in pipeline and other equipment. In fact, it also poses hazards to the environment and potential risks to human health [1]. At the present time, more natural gases contain H₂S is being produced in Malaysia as the consumption of natural gas is gradually increased. Total natural gas consumption is expected to grow at 18% annually between 2007 and 2035 [2].

Table 1 Range of acid gas composition (mole %) in typical refineries [3]

Components	Range of Composition (mole %)
CO ₂	3.60 - 74.41
H ₂ S	10.1 - 92.40
CH ₄	0.10 - 0.34
H ₂ O	6.30 - 3.25
C ₂ H ₆	0.10 - 0.02
C ₃ H ₈	0.15
CO	1.70
H ₂	0.66
N ₂	0.24 - 1.30

Recently, concerns over H₂S emissions from acid gas continue to draw ever increasing consideration towards the development of alternative sulfur recovery technology. The conversion of H₂S to a commercial product is an effort to reduce its emissions. Typical acid gas composition coming from refineries is shown in Table 1.

There are several technologies for sulfur recovery such as Claus and Wet Gas Sulfuric Acid (WSA) processes. The Claus process has been known for decades and has been used in industries to convert H₂S into elemental sulfur. The majority usage of this elemental sulfur is sulfuric acid plants. Thus, an alternative to directly convert H₂S into sulfuric acid is found in a technology called Wet gas Sulfuric Acid (WSA), developed by Haldor Topsoe. The WSA process has been found to be an efficient process for the production of concentrated sulfuric acid from acid gas [4].

From a sustainability point of view, it is very important to reduce this H₂S emission while at the same time producing a more useful product in a safer and more eco-friendly way. In this regard, a concept of 3P's (People, Planet, Profit) has been used as three important pillars of sustainability [5, 6]. The first pillar ("People") means that it is a safer process, while "Planet" symbolizes a more environmentally friendly process, and lastly, "Profit" means that the process itself has to make a profit in order to sustain.

Despite the presence of these two state-of-the-art technologies, acid gas comes with various capacities and H₂S concentrations. This research work aims to technically

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evaluate which of these two technologies suits better at which capacities and concentrations. To have a correct benchmarking metric, the above-mentioned sustainability pillars are used. In this research, the “People” pillar is indicated by well-known safety indices such as Fire and Explosion Damage Index (FEDI) and Toxicity Damage Index (TDI) via a Hazard Identification and Risk Assessment (HIRA) study is used [7, 8]. This safety assessment considers the chemicals used and the operating conditions of the process. For the “Planet” pillar, Global Warming Potential (GWP) is selected as the index for the environmental impact. Lastly and obviously, the annual profit of the process is taken as the “Profit” pillar.

In this work, both Claus and WSA processes modelled and simulated using a process simulation software called Symmetry-iCON. Based on the mass balance obtained from the simulations, the indices of FEDI, TDI, GWP, and annual profit are calculated accordingly. Due to the required granularities within the applicable range of capacities and concentrations, running smaller steps of variations is required. In this case, a surrogate approach of merging machine learning and first principles [9] is adopted. Thus, required simulation runs are obtained via a Design Of Experiment (DOE) using Central Composite Design (CCD) [10]. The data is then used to develop the surrogate models, which are then used to create a surface map for each

process in each index. Finally, surface maps of both processes are plotted together for each index for comparison.

2. RESEARCH AND METHODOLOGY

Figure 1 shows the overall methodology for this work where both Claus and WSA processes were modelled to calculate FEDI, TDI, GWP, and annual profit. CCD based simulation runs were then performed for the development of surrogate models. Then surface maps of the models were plotted for each index for comparisons.

The components taken in the simulation were hydrogen sulfide (H_2S), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), methane (CH_4), sulfur dioxide (SO_2), sulfur trioxide (SO_3), nitrogen (N_2), oxygen (O_2), hydrogen (H_2), sulfuric acid (H_2SO_4), and elemental sulfur (S_2 and S_8). Typical unit operations used in this simulation were furnaces, conversion reactors, heat exchangers, and separator vessels. In the WSA process, its condenser had three basic functions, namely a place to react (converting SO_3 to H_2SO_4), to reduce temperature and to condense (condensing SO_3 gas and H_2SO_4 gas to H_2SO_4 liquid), and to separate the gas from the condensed phase (separating liquid H_2SO_4 and clean gas) (11). In Symmetry-iCON, there is no WSA condenser unit per se available to do these three functions. Hence, this three equipment (conversion reactor, heat exchanger, and vessel) were used to simulate one WSA condenser.

Fig. 1. Research Methodology

In this project, H₂S concentration and feed gas capacity were varied as shown in Table 2 by using the CCD method. This method was used to minimize necessary simulation runs while still meeting enough variations to develop accurate regression or surrogate models for both WSA and Claus processes. These regression models were used further instead of 1st principles modelling from Symmetry-iCON due to their much faster calculations.

Table 2 Variation of feed capacity and H₂S concentration

No	Feed Capacity (kmol/hr)	H ₂ S Concentration Mole %
1	0.4095	4.29
2	0.4095	75.6
3	233	4.29
4	233	75.6
5	89.9	35.015
6	36.63	8.5
7	36.63	92.4
8	292.26	8.5
9	292.26	92.4
10	233	16.7

In each simulation, the operating conditions results obtained were then used to calculate the above-mentioned indices representing the three pillars of sustainability (3Ps). More details on how to calculate FEDI, TDI, GWP, and annual profit are taken in one of our previous works [12].

The regression models were developed as a function of two variables, namely feed capacity (x_1) and H₂S concentration (x_2). A general form of a second order regression model was used in this work. It is shown as follows.

$$Y = ax_1 + bx_2 + cx_1^2 + dx_2^2 + ex_1x_2 + f \quad (1)$$

Hence, there were four models developed for each Claus and WSA processes. The dependent variables (y) involve TDI, FEDI, GWP and annual profit as described above. Further details on the methodology and the subsequent results are covered in the literature [13].

3. RESULTS AND DISCUSSION

WSA Process Simulations Description

In the WSA process, the feed air and acid gas are fed into a combustor, where there are various reactions occurred during the combustion process. The main reaction is the H₂S is converted to SO₂ and CH₄ is burnt into CO₂ since it was one of the main feed gas compositions.

The gas stream leaves the combustor at 842°C and is cooled at 430°C before entering the reactor. The stream enters three consecutive conversion reactors with different required temperatures of inlet streams. The reaction that occurred in the reactor is to convert SO₂ to SO₃, which is a highly exothermic reaction, in a step-wise manner. Reactions occurring in the combustor are as follows:

The reactions are conducted under an adiabatic condition. To achieve a high conversion the reaction is then cooled in heat exchangers before entering the next conversion reactor. This cooling process produces steam which can be sold and taken as part of the annual profit calculation. After the third conversion reactor, the process gas is cooled from 443 °C to the acid dew point temperature of 260 °C in the condenser, producing the sulfuric acid. Reactions happening in the condenser are:

In this manner, this process achieves current requirement of acid mist emissions of about 20 ppmv without depending on air dilution. The conversions of the three reactors are shown in Table 3.

Table 3 Conversion in WSA reactors [4]

Reactor	Conversion fraction
Reactor 1	0.7736
Reactor 2	0.9107
Reactor 3	0.947

The vapor sulfuric acid stream was then cooled in a heat exchanger by cooling water at 20 °C before entering a 3-phase separator. At this point, the condensation of sulfuric took place where the hot sulfuric acid was condensed into liquid phase as the expected product. The clean gas is released at the top of separator. The developed flowsheet of this WSA process is shown in Figure 2.

Claus Process Simulations Description

The Claus process is one of the most common processes for sulfur recovery from acid gas generated in oil and gas refining. Elemental sulfur (S) is the final product, produced from the reaction between H₂S and SO₂. The SO₂ itself is produced from the combustion of H₂S and O₂ in the furnace [14]. In this simulation, the considered elemental sulfur is S₂ and S₈. The reactions that occurred in the combustor are as follows:

Reactions in the first reactor are as follows:

Fig. 2. Simulation Flow Sheet of WSA process

Fig. 3. Simulation Flow Sheet of Claus process

Fig. 4. Regression model of profit (\$/hr) in Claus and WSA processes (a) side view and (b) top view

The outlet from this reactor was then cooled to 200 °C and separated from the gas stream as the product stream. The upper gas stream was sent to the second reactor after heated up to 240 °C. In this reactor some of the produced SO₂ reacts with H₂S to produce sulfur S₈. This product stream is cooled down and enters a second separator at 200 °C producing another S₈ according to the following reaction:

The outlet stream contained some of S₈, S₂ and H₂S is then sent to a heater to heat up before entering the last reactor at 215 °C. This reactor produces elemental sulfur S₈ as the final product according to the following reaction:

Three stages of reactors are used in series to increase the yield of recovery process. In addition, the steam is generated at 1 barg as Low-Pressure Steam (LPS) during the cooling down/condensed process. Simulation flow sheet of the Claus process is shown in Figure 3.

Evaluation of Operating Conditions

The steam production is used to calculate the profitability of both processes. WSA process generates High Pressure Steam (HPS) at 40 barg (270 °C) while Claus produces Low Pressure Steam (LPS) at 1 barg. HPS and LPS are worth 29.97 USD/ton and 29.29 USD/ton, respectively (15). Based on the simulation runs, regression/surrogate models of the profit functions (in \$/hr) for both WSA and Claus processes are developed as function of feed capacity (x₁) and H₂S concentration (x₂), shown as follows:

$$\text{Profit}_{\text{WSA}} = -3.5x_1 + 10.5x_2 + 0.016x_1^2 - 0.11x_2^2 + 0.045x_1x_2 - 15.58 \quad (16)$$

$$\text{Profit}_{\text{Claus}} = 1.88x_1 - 1.75x_2 - 0.00252x_1^2 - 0.0167x_2^2 + 0.0025x_1x_2 + 38.32 \quad (17)$$

The accuracies of these models are shown by their multiple R values (square root of R²). These multiple R values show how strong the relationship between the data and the model where 1 or 100% being the strongest. Thus, equation 16 and 17 have the values of 97% and 85%, respectively. These values are close to 100%, showing their reasonable accuracies.

Figure 4 show the plots of these surrogate models for both processes in terms of profitability (in \$/hr). It can be seen that for most of the H₂S concentrations and capacities, the WSA process (dark colour) is more profitable than the Claus process (light colour).

The reason why the WSA process is more profitable in most of the operating conditions is due to the exothermic reactions occurred in WSA process that allows for more high-pressure steam to be generated. However, there is a narrow region where the Claus process is more profitable, which is at the lower concentration range of H₂S. At this low concentration region, not enough high-pressure steam is

generated to outweigh the necessary capitals required to build such facilities.

Planet (Environment) Regression Analysis

Based on result of GWP calculation, regression models of WSA and Claus processes are developed also as a function of feed capacity (x₁) and H₂S concentration (x₂). They are shown as follows.

$$\text{GWP}_{\text{WSA}} = -0.0066x_1 - 0.207x_2 + 0.000022x_1^2 + 0.0016x_2^2 - 0.0000077x_1x_2 + 6.29 \quad (18)$$

$$\text{GWP}_{\text{Claus}} = -8.3 \cdot 10^{36}x_1 + 7.8 \cdot 10^{36}x_2 + 2.4 \cdot 10^{34}x_1^2 + 1.1 \cdot 10^{35}x_2^2 + 4.5 \cdot 10^{33}x_1x_2 + 4.6 \cdot 10^{38} \quad (19)$$

The multiple R values of equation 18 and 19 are 94% and 85%, respectively. The consistent lower values for the Claus process may suggest that the approach of using a generic 2nd order equation may not suitable for the Claus process. Nonetheless, a more appropriate model can be researched for the future work.

These models are plotted as shown in Figure 5. From these plots, WSA is seen to be more environmentally friendly through its lower GWP, if not the same (the mid part of the region).

People (Safety) Regression Analysis

The developed regression models for FEDI (Fire and Explosion Damage Index) are as follows:

$$\text{FEDI}_{\text{WSA}} = -0.21x_1 + 0.16x_2 + 0.00027x_1^2 - 0.0035x_2^2 + 0.0016x_1x_2 + 31.32 \quad (20)$$

$$\text{FEDI}_{\text{Claus}} = 12x_1 + 64.79x_2 - 0.049x_1^2 - 0.74x_2^2 + 0.027x_1x_2 + 32.54 \quad (21)$$

For equation 20 and 21, their multiple R values are 80% and 71%, respectively. For this FEDI criteria, both equations have the lowest relationship with the data. Nonetheless, they are reasonably good (> 70%). These values again suggest that the 2nd order equation may have to be revisit in the future work.

Figure 6 illustrates the plots of the regression models of the FEDI. Due to more efficient conversions of WSA process, the amount of flammable materials in the system is much lower. It can be seen from the plots as well that the higher the quantity of H₂S (its concentration and feed capacity), the higher the FEDI index.

Toxicity hazard models via TDI are shown as follows and the corresponding plots are shown in Figure 9.

$$\text{TDI}_{\text{WSA}} = 1.856x_1 + 10.2x_2 - 0.0055x_1^2 - 0.099x_2^2 + 0.02x_1x_2 - 53.54 \quad (22)$$

$$\text{TDI}_{\text{Claus}} = 1.98x_1 - 0.53x_2 - 0.0042x_1^2 + 0.013x_2^2 + 0.015x_1x_2 + 22.52 \quad (23)$$

The multiple R values for equation 22 and 23 are 94% and 99%, respectively. The values show an excellent representation of the data.

Fig. 5. Regression model of GWP in Claus and WSA processes (a) side view and (b) top view

Fig. 6. Regression model of FEDI in Claus and WSA processes (a) side view and (b) top view

Fig. 7. Regression model of TDI in Claus and WSA processes (a) side view and (b) top view

As shown in Figure 7, the WSA process has a higher TDI than the Claus process in the most part of the operating ranges. This is because the production of sulfuric acid that occurs in the WSA process, while it is not considered in the Claus process. In this regard, future work on comparing the same input and output of the processes are necessary.

Nonetheless, the current work has shown that in three sustainability indices, the WSA process seems to be more superior than the Claus process. In the most part of the operating conditions, the WSA process is more profitable, lower GWP, lower FEDI, and higher TDI. Future work should consider the Claus process to be integrated with a sulfuric acid plant, which can then be compared with the WSA process to get an apple-to-apple comparison.

4. CONCLUSIONS

In this work, Haldor Topsoe's Wet Gas Sulfuric Acid (WSA) and Claus processes were simulated using Symmetry-iCON as a 1st principles modelling tool. The resulted mass and energy balance were then used to assess the suitability of these processes in various feed gas capacity and H₂S concentrations. Three pillars of sustainability of people (safety), planet (environment), and profit were used as the comparison metrics. To account for more detailed comparisons, a huge number of simulation runs were needed. To do this much faster, regression models were developed from selected simulation runs via Central Composite Design (CCD) of Design of Experiment. The WSA process has been shown to be the more sustainable process for H₂S conversion at most of the concentrations and capacity ranges. To be more specific, the WSA process is more profitable, producing lower GWP index, lower FEDI, and higher TDI.

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