



Performance Assessment of a Sulphur Recovery Unit

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Abstract

A refinery plant in the middle east started its official production in 2020. All the refinery plant acidic gas is fed to the Sulphur recovery unit plant to produce sulphur and prevent any acidic emissions against environmental regulations. The Sulphur recovery unit was simulated via special package named SULSIM. The results were validated, then the simulation was used in case studies to understand some important parameters of Sulphur recovery plants. The effect of decreasing the combustion air inlet temperature, the effect of decreasing the Claus reactor 1 inlet temperature and the effect of decreasing the thermal reactor feed were studied. Decreasing combustion air outlet temperature on the thermal reactor decreases the thermal reactor burning temperature, increases the concentration of COS and CS₂ by-products. Decreasing Catalytic reactor 1 inlet temperature decreases the hydrolysis reactions of COS and CS₂ but increases the Sulphur conversion efficiency. Decreasing AAG feed to the thermal reactor decreases the waste heat boiler duty.

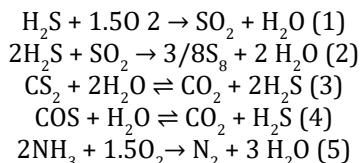
Keywords: Environmental; HYSYS; Simulation; Sulphur recovery unit; SULSIM

Abbreviations: AAG: Amine Acid Gas; ADA: Air Demand Analyzer; SRE: Sulphur Recovery Efficiency; SWS: Sour Water Stripper; SRU: Sulphur Recovery Unit; SWSAG: Sour Water Stripped Acid Gas; TGT: Tail Gas Treatment Section; TGTU: Tail Gas Treatment; WHB: Waste Heat Boiler.

Introduction

Hydrogen sulphide produced in the refinery industry is considered a hazardous pollutant as it has toxic and acidic nature [1-3]. Sulphur Recovery Unit (SRU) plants produce elemental Sulphur from Hydrogen Sulphide [4,5] and prevent any acidic gas emissions against environmental regulations in the world [6-8]. Claus process is one of the oldest methods to produce Sulphur from Hydrogen Sulphide. Several methods are used to increase Sulphur recovery but the modified Claus process is the most commonly used one. The concept of the process is that one-third of the H₂S contained in the acid gas feed is transformed into SO₂ in the Thermal Claus Section. SO₂ reacts with the remaining two-thirds of H₂S to form sulphur in the Catalyst Claus section [9-11]. The thermal section is

composed of a thermal reactor Claus furnace and a waste heat boiler (WHB) for heat recovery. In the thermal reactor, one-third of H₂S is oxidized through the reaction (Equation 1), in the catalytic section, the Claus reaction takes place to produce Sulphur by the reaction of remaining two-third of H₂S with SO₂ produced in the thermal reactor (Equation 2). The hot flue gas from Claus furnace containing also COS and CS₂ by-products is cooled in the WHB by water stream to produce high-pressure steam, and elemental sulphur is recovered after cooling in Sulphur condenser. Normally the Claus furnace performs (55-65%) H₂S conversion. The process gas out from the thermal section is reheated for the suitable temperature to perform Claus reaction producing Sulphur and hydrolysis reactions transforming COS and CS₂ to H₂S. The temperature is adjusted above sulphur dew point to prevent Sulphur condensation, then passed through the first catalytic reactor to produce sulphur by Claus reaction (Equation 2). The first catalytic reactor performs also hydrolysis reactions of COS and CS₂ through the reactions (Equation 3 and Equation 4).



A catalytic unit is composed of a reheater before the catalytic reactor and a condenser after the reactor. The maximum overall sulphur recovery efficiency (SRE) from thermal and catalytic sections is 93-95% for the 2-stage. SRE for the 3-stage catalytic units is limited to 96-98%. In recent years, SRE required to meet environmental regulations is

99.9% that can be achieved by the addition of the Tail Gas Treatment Unit (TGTU) to the modified Claus process [12-14].

A refinery plant in the middle east started its official production in 2020. All acidic gas from the refinery units is treated in the SRU plant. The SRU plant was simulated with Aspen HYSYS V.11 and many case studies were performed on the simulation to give a clear overview of the handling of SRU plants. The output from the plant simulation is shown in Figure 1.

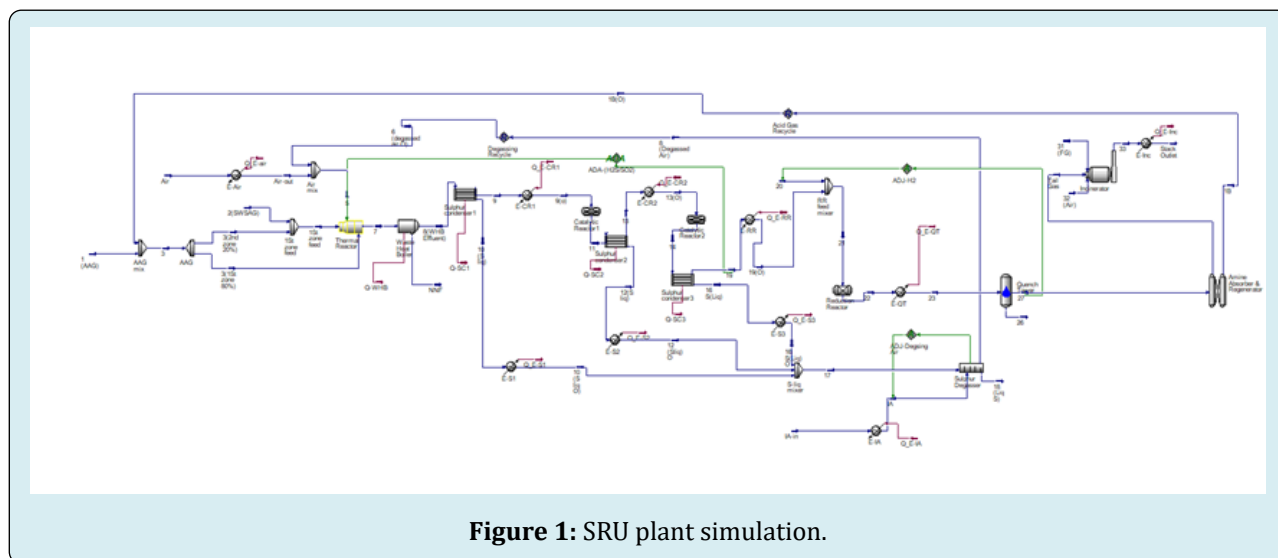


Figure 1: SRU plant simulation.

Process Description

The Sulphur Recovery Unit (SRU) and Tail Gas Treatment Unit (TGTU) are designed to recover sulphur from Amine Acid Gas and Sour Water Stripper Acid Gas. The SRU plant is composed from different sections. The SRU feed characteristics are shown in Table 1.

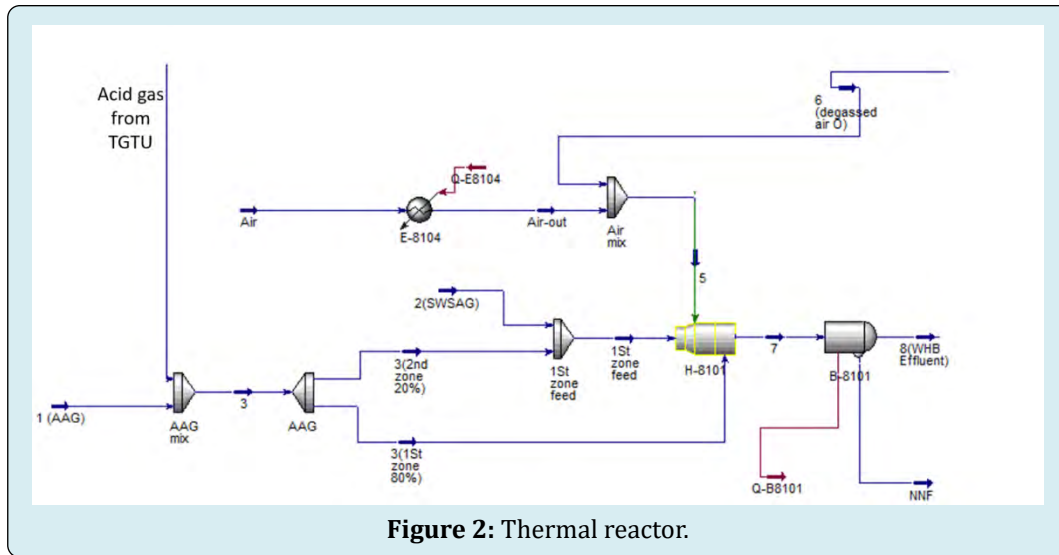
Claus Section

Claus section consists of Thermal Claus Section & Catalyst Claus section. The Claus process is used on acid gas streams containing essentially H_2S and CO_2 . The concept of the process is that one third of the H_2S contained in the acid gas feed is transformed to SO_2 in the Thermal Claus Section. SO_2 reacts with the remaining two third of H_2S to form sulphur in the Catalyst Claus section.

Thermal Reactor: The SWS Acid Gas is fed to the Main Burner of the Thermal Reactor with part of the Amine Acid Gas and the totality of combustion air. The complement of Amine Acid Gas is fed to the second zone of the Thermal Reactor, in order to maintain a minimum flame temperature in the first zone ensuring the NH_3 complete destruction. The flame temperature of the first zone is expected to be in the range between 1350°C and 1450°C adiabatic $\text{NH}_3/(\text{H}_2\text{S} + \text{NH}_3)$ ratio. The air to the Main Burner is exactly sufficient to accomplish the complete oxidation of all hydrocarbons and ammonia present in the total feed gases and to burn as much H_2S as required to obtain an $(\text{H}_2\text{S}/\text{SO}_2)$ ratio equal to 2:1 in the tail gas from Claus. The thermal reactor with WHB is shown in Figure 2.

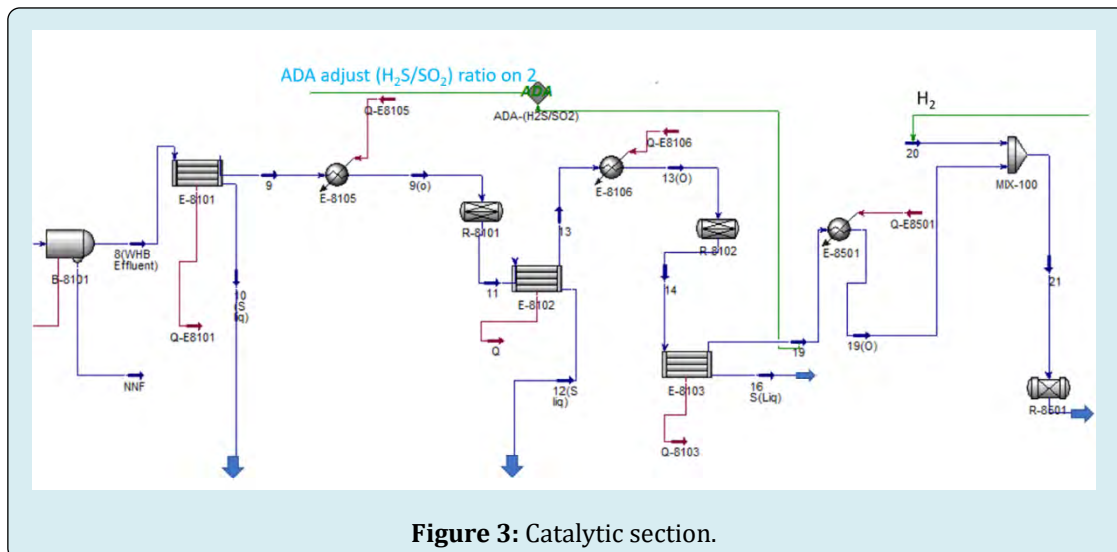
Stream Description		Amine Acid Gas	Sour Water Stripper Acid Gas
Property	Unit	Industrial	Industrial
Temperature	$^\circ\text{C}$	55	92
Pressure	$\text{Kg}/\text{cm}^2 \text{g}$	0.75	0.77
Flow	kg/h	11975	3674
Component		Mole fraction	
	H_2	0.003	0.000
	H_2O	0.083	0.339
	H_2S	0.912	0.334
	CH_4	0.001	0.000
	NH_3	-	0.327

Table 1: Sulphur recovery unit feed characteristics.



First and Second Claus Reactors: Before entering the Claus reactor, the process stream is indirectly heated to the optimum temperature for the catalytic conversion (about 240°C) in the first Reactor Reheater by means of high-pressure steam from Claus WHB. The reaction between H_2S and SO_2 in the Claus Reactor is accomplished till equilibrium over a catalyst bed; due to the exothermic reactions the gas leaving the Claus reactor has a temperature of about 300 °C. About 90% of the first Claus Reactor is filled with titanium (Ti) catalyst which enhances the hydrolysis reaction of COS and CS_2 . The effluent gas from the first Claus Reactor

is then routed to the second Sulphur Condenser where the Sulphur is condensed and drained via a Sulphur seal to the relevant Sulphur Drum. The process gas flow from the second Sulphur Condenser is again reheated by HP steam up to 200°C and fed to the second Claus Reactor, loaded with alumina catalyst. Approaching the turndown condition, it is suggested to raise preheating temperature at about 207°C in order to keep outlet tail gas slightly above the Sulphur dew point. The gas leaving the second Reactor enters the Final Sulphur Condenser before being sent to the TGT section. Figure shows the Figure 3.



Tail Gas Treatment Unit TGTU

Tail gas from the SRU shall be further treated in a single tail gas treating unit (TGTU) to improve the H_2S conversion to sulphur to 99.5wt%. Treat Claus tail gas from Claus

section to convert SO_2 into H_2S . The converted H_2S is cooled and then absorbed by lean amine then recycled to SRU feed to reprocessing. The tail gas treatment section is shown in Figure 4.

operation. This temperature is necessary to assure the nearly complete combustion of H_2S (less than 10 ppm residual H_2S is expected) and of other sulphur compounds contained in the tail gas. Figure 6 shows the incineration section.

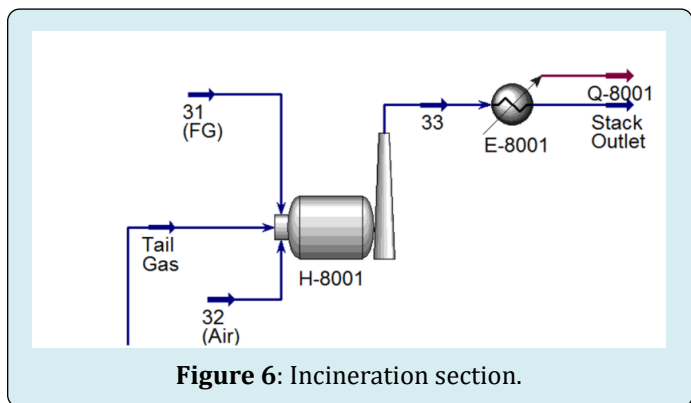


Figure 6: Incineration section.

Materials and Methods

Simulation Step

The study used Aspen HYSYS V.10 Sulphur SULSIM package for plant simulation. The simulation then was validated by comparison with plant data and then used in case studies.

Simulation Sections

The simulation consisted of different sections: (Claus, TGTU, degasser section and incinerator) sections.

Simulation of Claus Section: The reaction furnace empirical model is selected NH_3 SWS Acid Gas (Legacy): This is a legacy model commonly used for a plant that processes a sour water stripper (SWS) acid gas that contains significant amounts of ammonia (SWS acid gas stream contains 33% mole fraction ammonia), furnace type is selected two- chambers, other empirical models as (rich feed acid gas (legacy), lean feed acid gas (legacy), oxygen enrichment (legacy), straight through amine acid gas, SWS acid gas, split flow with lean acid gas, oxygen enrichment all acid gas, co-firing amine acid gas, co-firing SWS acid gas) are not suitable for this case. The 2 catalytic reactors are selected as catalytic converters, the

three Sulphur condensers are selected as Sulphur condensers. Sulphur condensers required information for definition are the inlet and outlet (temperatures and pressures). The catalyst selected in catalytic reactor1 is Titania catalyst. An ADA (Air Demand Analyzer) is controlling air flow to thermal reactor to adjust (H_2S/SO_2) in tail gas from catalytic section third condenser at a ratio of (2:1) as the optimum ratio for Sulphur conversion.

Simulation of Tail Gas Treatment Section (TGT): The tail gas treatment selected equipment is: (a quench tower, a simple amine absorber and regenerator. The reduction reactor is selected as hydrogenation bed. The hydrogen flow to reduction reactor adjust the hydrogen mole fraction outlet from the quench tower at a value of 0.2 mole fraction by an (adjust block). Recycle block is used for acid gas recycle from amine absorber and the regenerator to reaction furnace.

Simulation of Degasser and Incinerator: Degasser equipment is selected as (degassing), degasser outlet liquid Sulphur H_2S content of 10 ppm by weight is defined. Incinerator equipment is selected with the exact name in HYSYS. Incinerator target exit temperature is $652^\circ C$, target outlet O_2 mole fraction is 0.02. The defined parameters to the incinerator are tail gas, air and fuel gas inlet temperatures and pressures. A validation done for based case using industrial data to prove its ability to handle different situations.

Validation Step

Validation is done by comparing industrial data with simulation results. First, from the overall recovery efficiency point of view. Second, comparing between base case simulation and industrial data, the comparison concentrates on outlet product Sulphur stream and flue gases from stack stream because the aim of the plant is Sulphur production achieving environmental regulations. Third, outlet temperatures from reactors producing Sulphur (reaction furnace, catalytic reactor1 and catalytic reactor2) as they are a good indication about the performance of the reactors. The validation shows the simulation ability to handle plant test performance and process optimization efficiently. The validation results are shown in Table 2.

Stream Description		Liquid Sulphur Product			Flue Gas to Stack		
Property	Unit	Industrial	Simulation	% Error	Industrial	Simulation	% Error
Temperature	$^\circ C$	135	135	-	652	652	-
Pressure	kg/cm ² g	0.01	0.01	-	0.01	0.01	-
Flow	kg/h	12430	12438	0.1	41283	43002	4.2
Component		Mole fraction					

H ₂	0.000	0.000	0.0	0.012	0.011	8.3
H ₂ O	0.000	0.000	0.0	0.116	0.120	3.6
CO	0.000	0.000	0.0	0.000	0.000	0.0
N ₂	0.000	0.000	0.0	0.828	0.819	1.0
O ₂	0.000	0.000	0.0	0.020	0.020	1.4
CO ₂	0.000	0.000	0.0	0.025	0.023	5.3
S liq	1.000	1.000	0.0	0.000	0.000	0.0
NH ₃	0.000	0.000	0.0	0.000	0.000	0.0

Table 2: Validation results.

Results and Discussions

Effect of Decreasing Combustion Air Outlet Temperature on the Thermal Reactor

The combustion air is responsible to perform all the oxidation reactions in the thermal reactor. The design air temperature inlet to the thermal reactor is 240 °C. A case study is performed to see the effect of decreasing this

temperature on thermal reactor parameters. The reactor temperature decreased from 1349.12 °C to 1335.61 °C. Consequently, the concentration of by-products COS and CS₂ increased. Table 3 shows the Effect of decreasing combustion air outlet temperature on the thermal reactor. The COS concentration increased from 6.14 ppm-mol to 7.83 ppm-mol. The CS₂ concentration increased from 7.10 ppm-mol to 8.50 ppm-mol. The Sulphur conversion decreased from 69.09% to 69.05%.

Combustion Air T (°C)	Thermal Reactor Outlet T (°C)	Thermal Reactor Sulphur Conversion %	Thermal Reactor COS ppm-mol Outlet	Thermal Reactor CS ₂ ppm-mol Outlet
210	1335.61	69.05	7.83	8.5
217.5	1338.97	69.06	7.41	8.13
225	1342.34	69.07	6.99	7.77
232.5	1345.72	69.08	6.56	7.43
240	1349.12	69.09	6.14	7.1

Table 3: Effect of decreasing combustion air outlet temperature on the thermal reactor.

Figure 7 shows Effect of decreasing combustion air outlet temperature on the thermal reactor burner temperature.

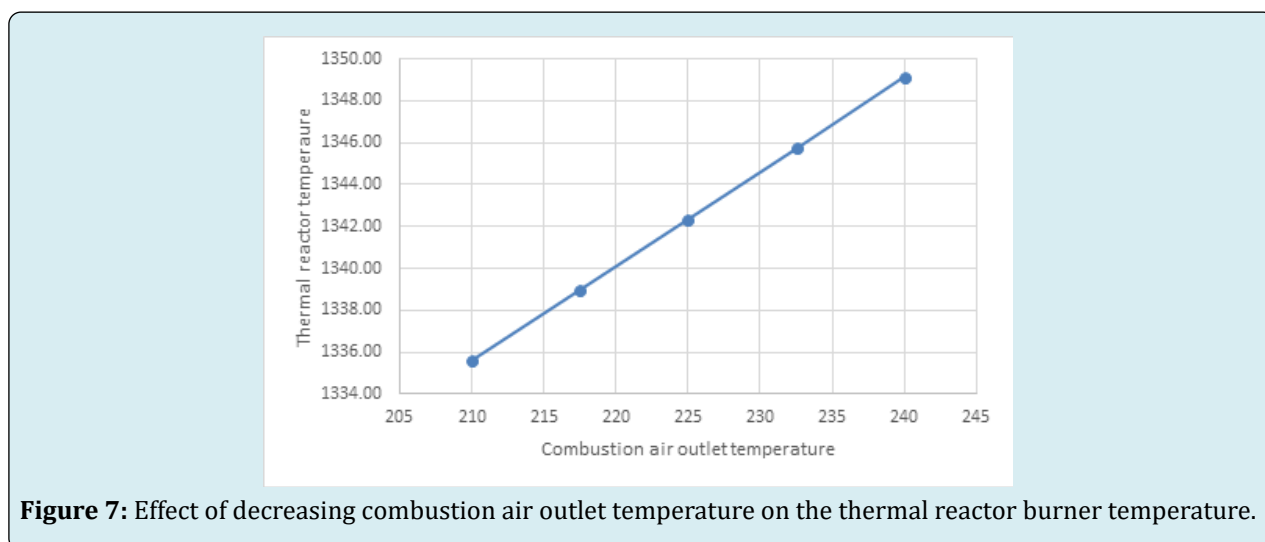


Figure 7: Effect of decreasing combustion air outlet temperature on the thermal reactor burner temperature.

Effect of Decreasing Catalytic Reactor 1 Inlet Temperature

The decreasing of catalytic reactor 1 inlet temperature from 240°C to 210°C decreases the hydrolysis reaction of COS from 99.04% to 98.34% and decreased CS₂ hydrolysis

from 92.67% to 86.88%. While the Sulphur conversion efficiency increased from 71.02% to 77.82% because the Claus reaction performance is better on lower temperatures. The effect of decreasing Catalytic reactor 1 inlet temperature is shown in Table 4.

Catalytic Reactor 1 Inlet T (°c)	Catalytic Reactor 1 COS Hydrolysis Result %	Catalytic Reactor 1 CS ₂ Hydrolysis Result%	Catalytic Reactor 1 Sulphur Conversion Efficiency%
210	98.34	86.88	77.82
217.5	98.6	88.71	76.2
225	98.79	90.26	74.52
232.5	98.94	91.57	72.79
240	99.04	92.67	71.02

Table 4: Effect of decreasing Catalytic reactor 1 inlet temperature.

Figure 8 shows the decrease of Sulphur conversion efficiency by the higher temperatures.

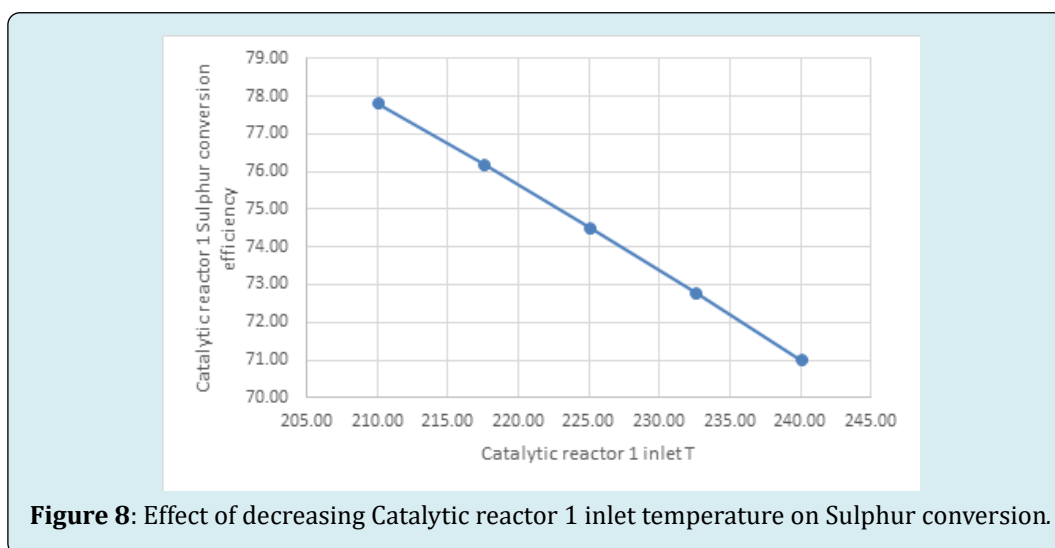


Figure 8: Effect of decreasing Catalytic reactor 1 inlet temperature on Sulphur conversion.

Effect of decreasing the AAG feed to the thermal reactor on the WHB duty

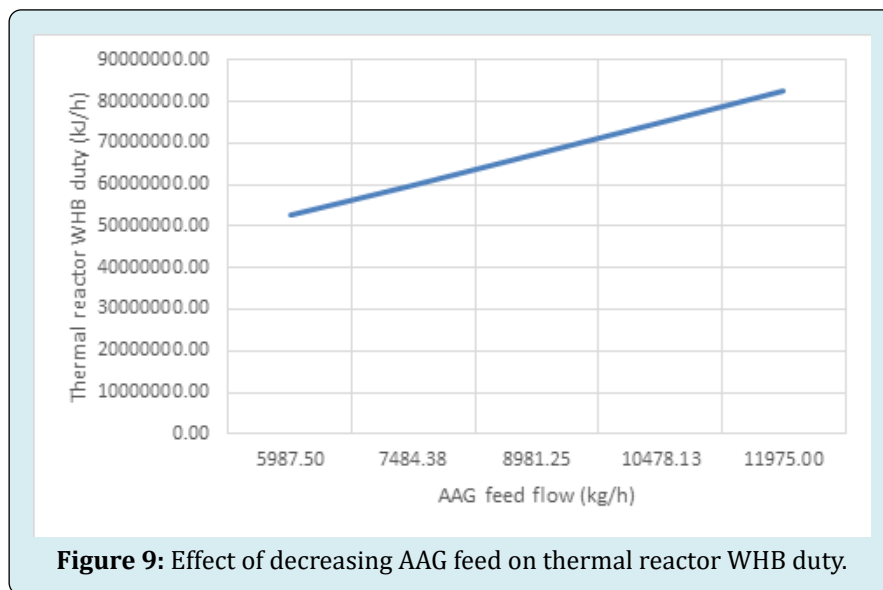
Decreasing the AAG feed to the thermal reactor decreases

the WHB duty from 82301625.34kJ/h to 52587827.42 kJ/h as shown in Table 5. This means that steam production from the WHB will be decreased also.

AAG Feed Mass Flow (kg/h)	WHB duty (kJ/h)
5987.5	52587827
7484.38	60003631
8981.25	67459477
10478.13	74914338
11975	82301625

Table 5: Effect of decreasing AAG feed to thermal reactor on thermal reactor WHB duty.

Figure 9 shows this relation.



Summary and Conclusions

A Sulphur recover unit of a refinery plant was simulated using a special HYSYS package named SULSIM. The results were validated and compared with industrial data. Then case studies are performed to understand the SRU performance. decreasing combustion air outlet temperature on the thermal reactor from 240 °C to 210 °C decreases the thermal reactor burner temperature from 1349.12 °C to 1335.61, increases the concentration of COS by-product from 6.14 ppm-mol to 7.83 ppm-mol, increases the concentration of COS by-product from 7.10 ppm-mol to 8.50 ppm-mol and decreases the Sulphur conversion from 69.09% to 69.05%. Decreasing catalytic reactor inlet temperature from 240 oC to 210 °C decreases the hydrolysis reaction of COS from 99.04% to 98.34%, decreases CS₂ hydrolysis from 92.67% to 86.88% but increases the Sulphur conversion efficiency increased from 71.02% to 77.82% because the Claus reaction performance is better on lower temperatures. Decreasing the AAG feed to the thermal reactor from 11975.00 kg/h to 5987.50 kg/h decreases the thermal reactor WHB duty from 82301625.34 kJ/h to 52587827.42 kJ/h.

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