

## PROCESS SIMULATION AND OPTIMIZATION OF CATALYTIC REACTORS OF SULFUR RECOVERY UNIT (SRU) VIA ASPEN PLUS

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### **Abstract**

In this study, the solid package of Aspen plus is applied for simulating and optimizing temperatures of Claus convertors in an industrial scale sulfur recovery unit (SRU). At first, to prove the accuracy of the simulator developed for the target SRU, H<sub>2</sub>S conversion and rate of sulfur production which are calculated by Aspen plus, are compared with design data. It is observed that Aspen plus can predict the total H<sub>2</sub>S conversion of the process with the absolute average deviation (AAD%) of 1.59% at the average reaction temperature. Moreover, the total sulfur production rate of the plant can be simulated with the AAD% of 10.22%. From these results, it is concluded that the simulator is reliable to be applied for optimizing temperatures of Claus convertors in the target process. After performing the sensitivity analysis, it is shown that by decreasing the average temperatures of 2nd and 3rd convertors from 213.9°C and 199°C to 205°C and 190°C, respectively, the H<sub>2</sub>S conversion increases about 1.2% which is significant to decrease the emission of this harmful compound.

**Keywords:** *Claus process; Simulation; Aspen plus; Optimization; Sulfur.*

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## **1. Introduction**

Hydrogen sulfide (H<sub>2</sub>S) is a toxic gas, and it is so harmful to live issues; therefore, its present in the exhaust gas of oil and gas refineries are under strict environmental regulations. The modified sulfur recovery unit (SRU) is favorably used to transform H<sub>2</sub>S into elemental sulfur [1-3]. This product is an extremely useful element, and its largest application is for the manufacture of fertilizers with other principal users including rubber industries, cosmetics, and pharmaceuticals [4]. Consequently, SRU is momentous from economic and environmental aspects.

Respect to the simulation of a catalytic section of the modified Claus process, there are scarce studies reported in the literature. Asadi *et al.* [5] have studied the effect of H<sub>2</sub>S concentration on the reaction furnace temperature and sulfur recovery. First, the simulation of Claus process was considered using a process simulator called TSWEET, and then the effect of H<sub>2</sub>S concentration and H<sub>2</sub>S/CO<sub>2</sub> ratio in three different concentrations of oxygen (in input air into the unit) on the main burner temperature and sulfur recovery were studied and compared. Also, in this paper, it was shown that recovery rate of sulfur increases up to a maximum value, and then decreased as H<sub>2</sub>S concentration and H<sub>2</sub>S/CO<sub>2</sub> ratio (in all three concentrations of oxygen) increased. In the other work, Pahlavan *et al.* [6] simulated the reaction furnace of a Claus process using a kinetic based model. The predicted outlet temperature and concentrations by this model were compared with experimental data published in the literature, and also data obtained by PROMAX V2.0 simulator. The results demonstrated that the accuracy of the proposed kinetic model and its simulator were almost similar. Nabgan *et al.* [7] proposed a simulation for a Claus process plant via Aspen HYSYS V8.8 simulator. In this study, it was shown that only factors which could affect the conversion of H<sub>2</sub>S were the feed composition and its molar flow rate. Eghbal Ahmadi [8] simulated the Claus process based on simultaneous data reconciliation and parameter estimation. The Claus process was characterized by several

problems for predicting the behavior of the reactors. In this paper, industrial plant was simulated using Hysys software based on simultaneous data reconciliation and parameter estimation using a Genetic algorithm (GA). Analysis of the results proved that the standard deviation of the reconciled data was reasonably reduced comparing with their raw measured values. Accordingly, measuring errors caused by various unfavorable problems in the plant such as instrumentation inaccuracy were reduced. Having developed simulation model with accurate values of process variables, the behavior of the plant was precisely monitored. Moreover, the developed simulation model could be used for process optimization and control purposes.

In the present study, the capability of Aspen plus to simulate the conversion of  $H_2S$  and carbon-sulfur compounds are studied. The results are validated versus the design data provided by the licensor of the target SRU. After validating the simulation, the temperature of the catalytic Claus reactors are optimized, and the effect of the recommended operating conditions on the conversion of  $H_2S$  is reported. Due to the importance of the SRU from the environmental view point, this research and the proposed methodology can be significant.

## 2. Process description

Sour Gas is routed through the sour gas separator D-101 to heat exchanger E-101. A schematic process flow diagram of Claus process unit is shown in Figure 1.

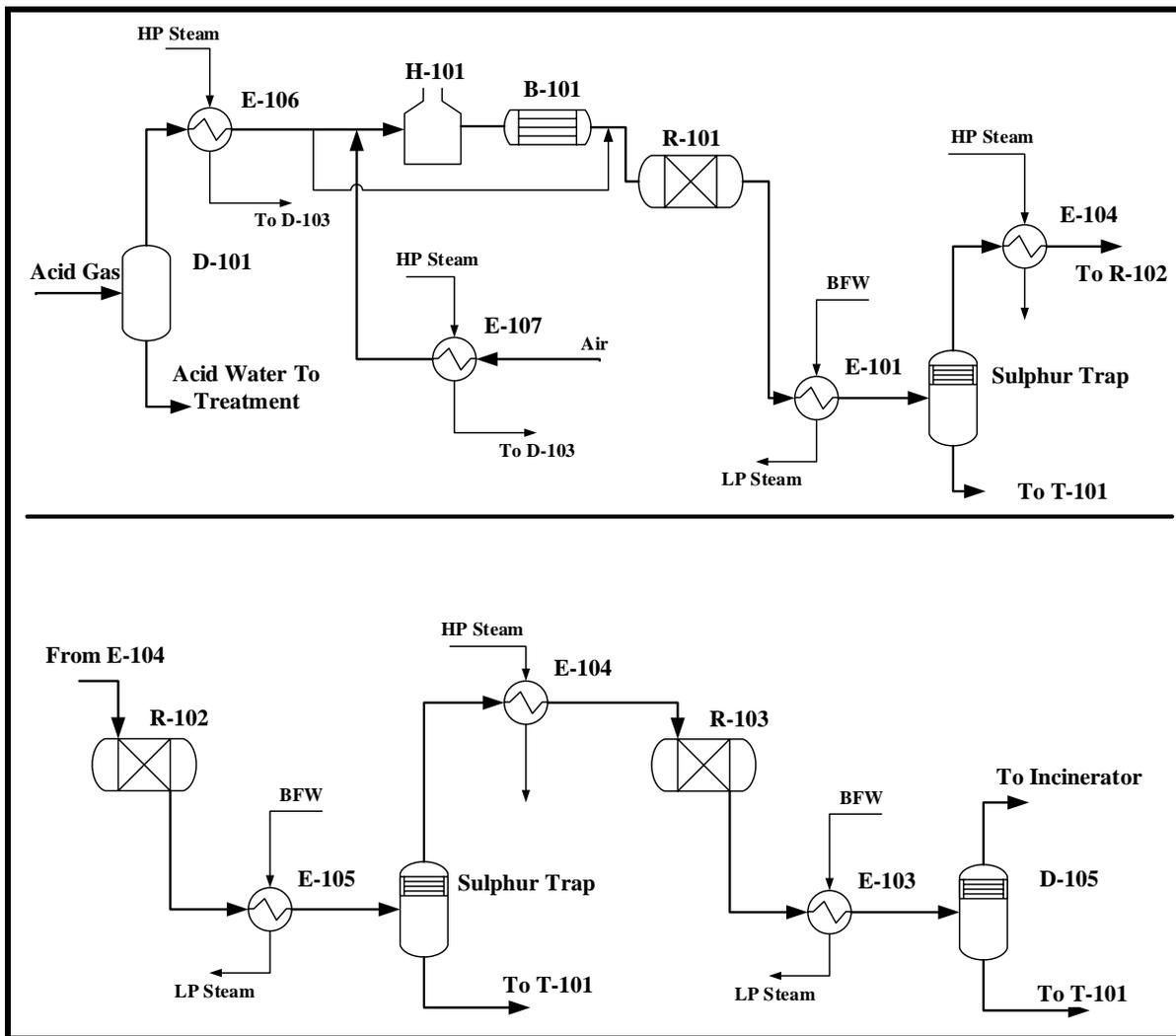


Figure 1. Process flow diagram of Claus process unit

If water precipitates in D-101, it will be routed to the slop drum by means of the sour water pump. The central muffle is used to combust fuel gas for heating purposes during start-up, shutdown or low-load. The size of the combustion chamber H-101 is selected so as to approximately reach the thermodynamic equilibrium in the off gases from the central muffle and the H<sub>2</sub>S-burners. Many chemical reactions taking place in the combustion chamber H-101 transform part of the H<sub>2</sub>S into sulfur vapor.

Directly connected to the combustion chamber, H-101 is the Claus process gas cooler B-101 with the steam drum, which serves to cool the process gas from about 1009°C to about 250°C and precipitate part of the sulfur vapor. To control the gas temperature to the first Claus reactor R-101, part of the process gas is sent directly through Claus process gas cooler B-101 via a central pipe to a Claus mixing valve, which mixes the cooled gas with the hot gas. After leaving the Claus mixing valve, the process gas is routed to the first Claus reactor R-101. Here the sulfur components are further converted into elemental sulfur over a catalytic bed. The extent of conversion depends on prevailing temperature in this reactor. The reactor has an outlet temperature of approximately 325°C. After leaving the first Claus reactor R-101, the process gas enters the first sulfur condenser E-101 with the steam drum, which serves to cool the process gas to about 175°C and precipitates part of the sulfur vapor. The gas leaving the first sulfur condenser E-101 has to be heated to the inlet temperature of the second Claus reactor (205°C). In the second Claus reactor, R-102 converts the remaining sulfur compounds to elemental sulfur. The process gas leaves the second Claus reactor with a temperature of approximately 229°C and is cooled to about 130°C in the downstream second sulfur condenser E-105 to precipitate most of the sulfur vapor. Before the process gas is routed to the section for further treatment, it passes the sulfur separator D-105 where entrained liquid sulfur is separated from the gas stream.

### 3. Simulation methodology

#### 3.1. Feed specifications

The specifications of the feed introduced to the first reactor of the target SRU unit are presented in Table 1.

Table 1. Specifications of the feed entered into the first catalytic reactor

	Value		Value
Mole flow (kmol/h)	1.77	Pressure (bara)	1.38
Temperature (°C)	250		
Composition (mol%)			
H <sub>2</sub> S	3.61	CO	1.77
SO <sub>2</sub>	2.86	CO <sub>2</sub>	24.30
H <sub>2</sub> O	25.24	H <sub>2</sub>	1.03
COS	1.91	N <sub>2</sub>	38.97
CS <sub>2</sub>	0.17	S <sub>5</sub> to S <sub>8</sub>	0.13

The feed of the catalytic bed and also produced sulfur exited from the SRU convertors mostly included sulfur with 8 atoms (Octa-sulfur, the common allotrope of sulfur). Therefore, to simplify the simulation, all allotrope of sulfur (i.e., S<sub>2</sub> to S<sub>8</sub>) is lumped as the S<sub>8</sub> compound.

#### 3.2. Simulation of SRU convertors

Aspen Plus (Aspen Tech, V7.2) can simulate the process in which solids are produced, or they should be handled. In this simulator, a wide range of unit operation models are provided for solid operations. In this study, to simulate catalytic reactors of SRU process, REquil model which is available in the model library of the Aspen Plus is applied. REquil models reactors when reactions meet the equilibrium. This module can calculate single phase chemical equilibrium, or simultaneous phase and chemical equilibria. Moreover, REquil is capable of calculating equilibrium by solving stoichiometric chemical and equilibrium state equations. To do this task, it is assumed that the following equations are carried out in the SRU convertors:



Since properties of sulfur and other phases cannot be estimated with the same type of models, produced sulfur is distributed over the other sub stream, and its properties are calculated by using Solid package. Additionally, the S8 product exited from each catalytic reactor is separated from the other components using a component separator (Sep module).

#### 4. Results and discussions

##### 4.1. Validation of SRU simulation

Based on the design data and the described methodology, the target sulfur recovery facility was simulated in the Aspen plus (see Fig.2).

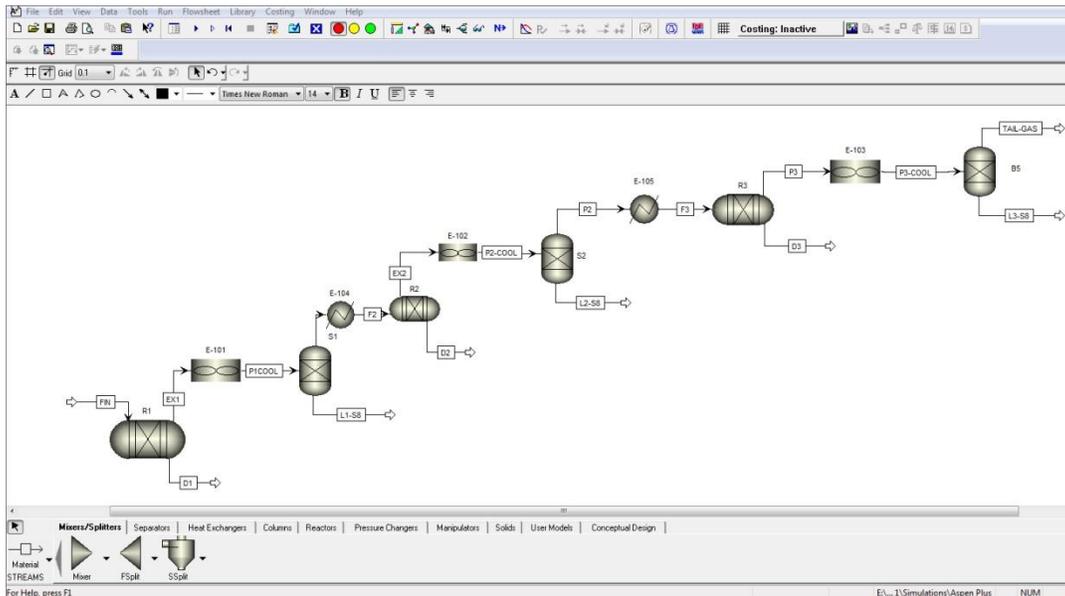


Figure 2. Process flowsheet for simulating SRU catalytic convertors in Aspen plus

The absolute average deviation (AAD%) of simulated data against the design data for total H<sub>2</sub>S, CS<sub>2</sub>, and COS conversions are shown in Table 2. These data confirm that the flowsheet simulation developed in Aspen plus for the target Claus process can satisfactorily calculate the main output variables of the process and it can be used for analyzing this process. As observed, such as the total conversions, Aspen model can appreciably predict these output variables with acceptable accuracy.

Table 2 Comparison of simulation results and design data for H<sub>2</sub>S, COS, and CS<sub>2</sub> conversion

Conversion	Design	Simulation	AAD%
H <sub>2</sub> S (mol%)	93.94	92.44	1.59
COS (mol%)	94.8	99.99	5.48
CS <sub>2</sub> (mol%)	90.2	100.00	10.86

To have a better justification, comparisons between the simulated sulfur production versus design data are illustrated Figure 3. As observed, such as the total conversions, Aspen model can appreciably predict these output variables with an acceptable accuracy.

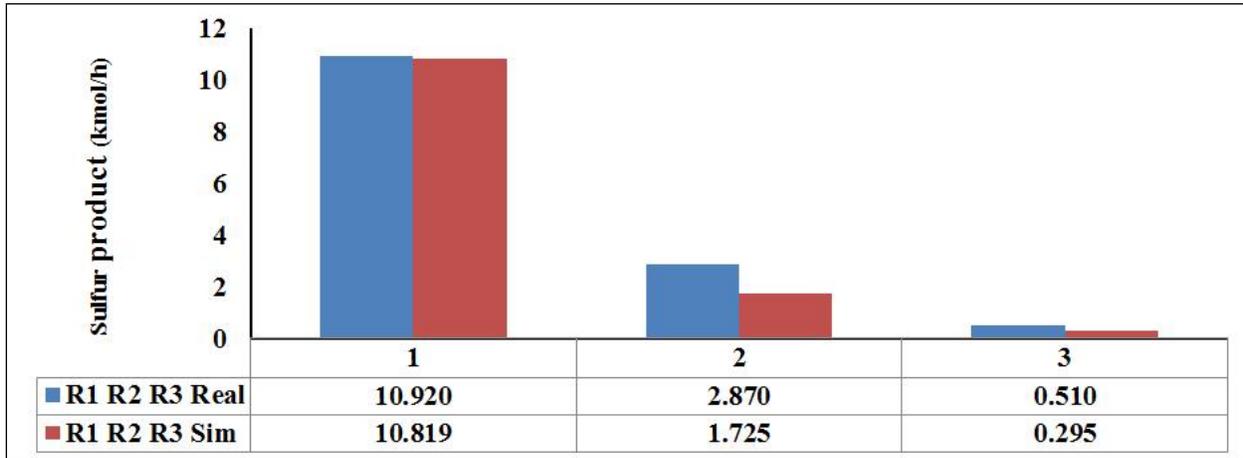


Figure 3. Comparison of simulation results and design data for sulfur production

#### 4.2. Sensitivity analysis for SRU simulation

After validating the SRU simulator, the sensitivity analysis of the H<sub>2</sub>S conversion to average bed temperature for 1st, 2nd, and 3rd catalytic convertors are presented in Figs 4 to 6, respectively. As seen from these figures, by increasing the average temperature of beds, the H<sub>2</sub>S conversion decreases sharply. This phenomenon is expectable due to the exothermic nature of the Claus reactions; therefore, a cooler and condenser is provided between catalytic beds for decreasing the temperature and also removing the produced sulfur from the gas stream. If the partial pressure of sulfur increases through the catalytic beds, pore plugging due to the capillary condensation of sulfur will happen; consequently, the catalyst will be deactivated fast. Sulfur molecules formed during the Claus reactions can plug pores of catalyst even at a temperature higher than sulfur dew point temperature.

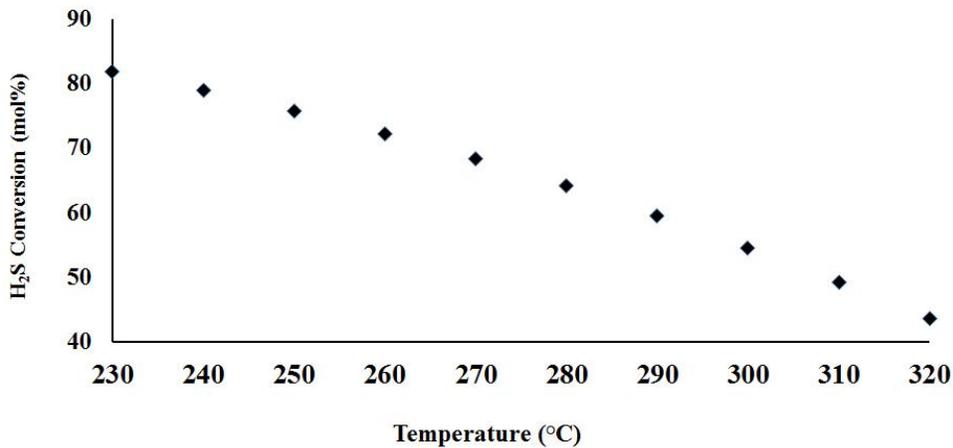


Figure 4. Total conversion of H<sub>2</sub>S as a function of average temperature in the 1st catalytic convertor

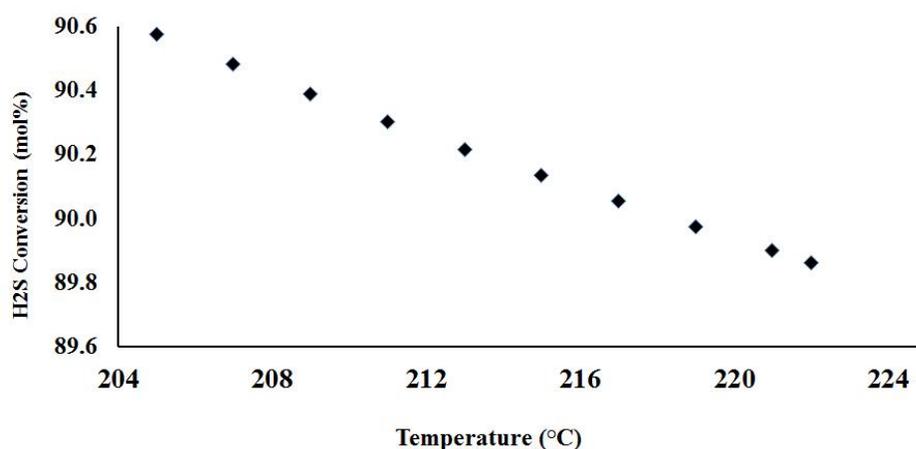


Figure 5. Total conversion of H<sub>2</sub>S as a function of average temperature in the 2nd catalytic converter

It should be noted that the first converter is more sensitive to the temperature because of the high partial pressure of H<sub>2</sub>S, and also higher operating temperature. In the 1st catalytic reactor, a layer of promoted pure titanium oxide (titania or TiO<sub>2</sub>) sulfur recovery catalyst after the first layer (activated alumina catalyst) is provided. This catalytic bed is considered for total hydrolysis of COS and CS<sub>2</sub> compounds which their corresponding reactions promote at a temperature higher than 280°C, preferably 300°C.

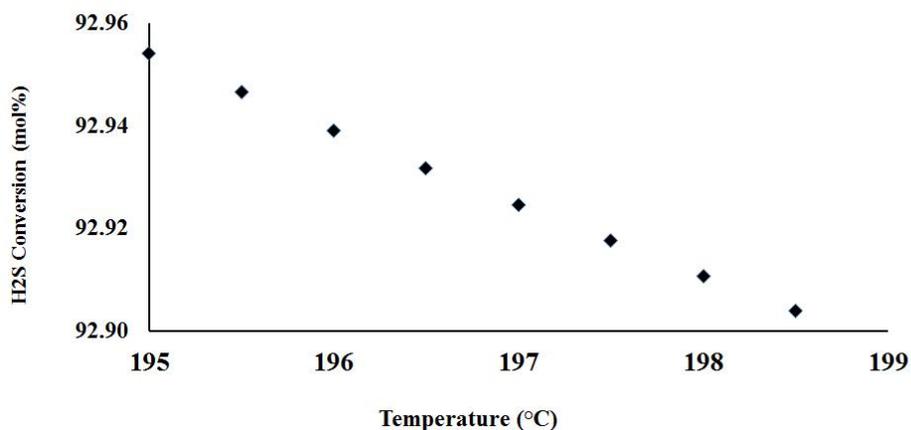


Figure 6. Total conversion of H<sub>2</sub>S as a function of average temperature in the 3rd catalytic converter

#### 4.3. Optimizing temperatures of SRU catalytic reactors

For determining optimum operating conditions, it is recommended that the average temperatures of the 2nd and 3rd converter can be meticulously decreased. Therefore, by reducing these temperatures, higher H<sub>2</sub>S conversion and lower emission can be expected. Due to the importance of the hydrolysis reactions carried out in the second catalytic layer of the 1st reactor (as described before), the average temperature of the first converter is not included in the optimization program.

If the target SRU currently operates at average bed temperatures of 214°C and 199°C, respectively, these temperatures can be slightly reduced. In Figure 7, variations of H<sub>2</sub>S conversion versus temperature reduction in average bed temperature of 2nd and 3rd reactors are depicted. As seen, up to 2°C temperature reduction, no significant total H<sub>2</sub>S conversion of the plant has been observed. After this point, for each degree centigrade reduction in bed tempe-

ratures, about 0.1 mol% increase in the H<sub>2</sub>S conversion is expected. If the temperature can be reduced to 205°C and 190°C for 2nd and 3rd convertors, respectively, about 1% in H<sub>2</sub>S conversion is accessible which is equal to 4% decrease in the H<sub>2</sub>S emission.

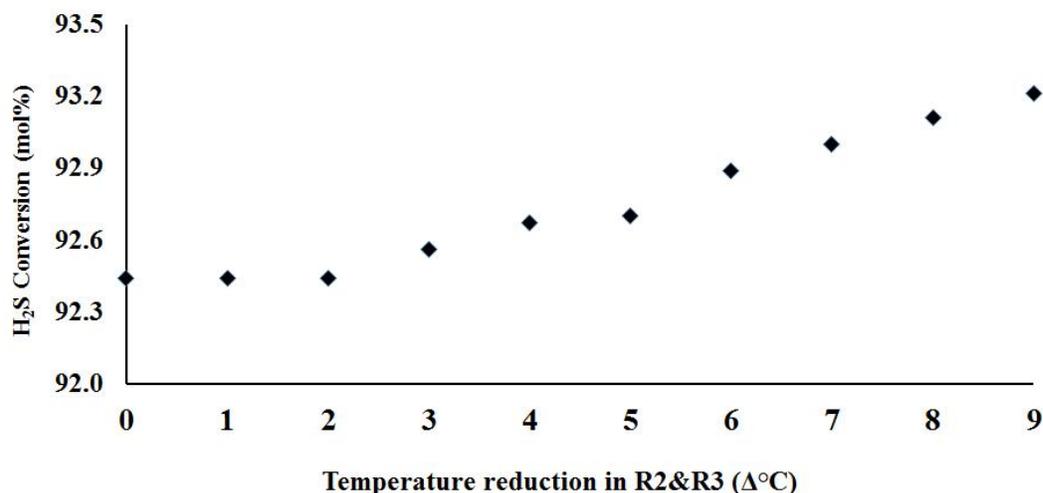


Figure 7. Variations in the total conversion of H<sub>2</sub>S vs. temperature reduction of the 2<sup>nd</sup> and 3<sup>rd</sup> convertors

## 5. Conclusions

In this present research, it was demonstrated that Equilibrium reactor (REQUIL) and solid package provided in Aspen plus simulator could be successfully used to simulate Claus convertors of an SRU. In this industrial scale plant, three catalytic reactors were provided to convert H<sub>2</sub>S and carbon sulfide compounds (i.e., COS and CS<sub>2</sub>) to the sulfur (mainly 8-atomic). It was concluded that Aspen plus could calculate the H<sub>2</sub>S conversion of the 1st, 2nd and 3rd catalytic reactors with the accuracy of 22.19%, 0.59%, and 1.59%, respectively. The higher deviation of the simulation for the first reactor was mainly due to the multi-layers of alumina and titania catalyst loaded in that for converting H<sub>2</sub>S and hydrolysis of carbon sulfur compounds and, simultaneously. Additionally, based on the designed operating conditions, the rate of the sulfur product calculated by Aspen plus was 12.84 ton/h closed to the design value which was supposed to be 14.3 ton/h.

After validating the SRU simulator, results confirmed that 5°C decrement in the average temperatures of the 2nd and 3rd convertors could increase the total conversion of H<sub>2</sub>S from 92.67 mol% to 93.21 mol% due to the exothermic nature of the Claus reactions. Because the 1<sup>st</sup> reactor was designed to hydrolysis COS and CS<sub>2</sub>, and these reactions were substantially promoted at a temperature higher than 300°C, decreasing the temperature of this convertor was not recommended.

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