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An Aspen HYSYS Model for Replacing Dimethyl Disulfide with Disulfide Oil

Erfan Ziarifar*, **Rahbar Rahimi, Morteza Zivdar**

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Abstract

This research was carried out to simulate of Replacing Dimethyl Disulfide (DMDS) with Disulfide Oil (DSO) using Aspen HYSYS. In this paper, injection of DSO issimulated. The simulation is based on cracking hydrocarbons such as ethane and methane in the pilot.By simulating and installing this pilot before the furnace, 99.99% hydrogen sulfide is gained and the other sulfur-containing materials, mercaptans, etc. do not remain in the furnace. The simulation results the 99% H2Sconversion of DSO in outlet stream. The model is able to predict the conversion rate of sulfur material to H2S in outlet stream.Finally, GC (gas chromatography) analysis was carried out and compared with the simulation to validate the model and to perform the case study calculations.The reactorof set upis modeled with Gibbs reactor. The results of simulation are validated against calculated data from GC results on built pilot's composition in the feedare also found to decrease with temperature increasing at 800 °C and converted to H2S completely. First step of this study is the development of Cracking with DSO Process using Aspen HYSYS version 8.8 and comparing the model's results with GC analysis ofAmir Kabir Company's results.Experimental data from the DSO Pilot were used as a basis to perform the process simulation using Aspen HYSYS.

Keywords: DSO, H2S, Olefin, Process Simulation, Aspen HYSYS

Introduction

Process description

Steam cracking is still the most reliable and efficient commercial process for the production of light olefins, specifically ethylene. Cracking of hydrocarbon ranging from ethane to gasoil is the main source of olefin production. One of the main problems of steam cracking is the formation of carbonaceous material (coke) inside the radiant tube ((Sadrameli, 2016; Eletskii and et al, 2016; Usman and et al, 2017; Corma and et al, 2018). In olefin production using steam, a carbonaceous material is deposited at the inner wall of the cracker coils (tubes) (Amghizar and et al, 2017; Su and et al, 2016). In industrial olefin plants, additives are used to control coke production and inhibit coke formation inside the coil system. Recently extensive research has been conducted on coke formation during cracking of different hydrocarbons such as ethane, propane, n-hexane, and naphtha.Sulfur-containing compounds (such DMDS) are injected into the cracking furnace and result in the production of coke by covering the inner surfaces of the heat pipes at higher temperatures (Baghmishe and Dorosti, 2016; Arystanbekova and et al, 2017l Yamaguchi and et al, 2015). An expensive chemical used in the olefinplants is "Dimethyl Disulfide" (DMDS).In this paper, simulation of replacing Dimethyl Disulfide with DSO is studied. One of the reasons for selecting this alternative was the lower cost of DSO as compared to DMDS.The coil outlet temperature and the pressure inside these pipes affect the conversion product (Towfighi and et al, 2002; Mironenko and et al, 2017; Hussain and et al, 2016).

Materials and Methods

DMDS

DMDS is used in furnaces and heaters to reduce the coke formation (López García and et al, 2002). DMDS is a pale-yellow liquid with the vapor pressure of 29 mmHg at 25 °C and water solubility of 3 g/L at 20 °C. DMDS has a garlic-like or sulfurous odor and it is approved as a food additive in the USA .Itis used in all of the olefin petrochemical units (under the license of Linde Company). H2S functions as an inhibitor in the coke formation process. This substance is obtained from various sources, but in the case of thermal cracking in olefin units, it is obtained from DMDS (López García and et al, 2002; Woerde and et al, 2002; Goswami & Kumar, 2014,

Erfan Ziarifar*
PhD student, School of Graduate Studies, University of Sistan and Baluchestan, Zahedan, Iran

Rahbar Rahimi, Morteza Zivdar
Chemical Engineering Department, University of Sistan and Baluchestan, Zahedan, Iran

*** Email:** ziarifar@pgs.usb.ac.ir

Eltejaei and et al, 2012).;

The quantitative release of H2S starts at different temperatures and is completed at various times for different sulfurizing agents (Rahimi and et al, 2014).

DSO

DSO contains various substances such as DMDS, DEDS (diethyl disulfide), and EMDS (ethyl methyl disulfide).For the purpose of this research, DSO was stored at the 25 ℃ temperature under atmospheric pressure conditions in a special container. The present research was carried out on a substance named DSO, which is burned in most refineries as waste. If DSO had been injected into the furnace under the same conditions, the residence time would have led to numerous problems such as an increase in the sulfur content of the intermediate products such as pyrolysis gasoline. However, in the pilot experiment, DSO was preheated up to a temperature of 800℃ , and finally it was injected into the heat pipes (coils) of an olefin furnace at 1000 ℃ (Taheri and et al, 2008; Yuan and et al, 2016; Salari and et al, 2006).

Present scheme of DSO pilot

In this paper, a semi-industrial pilot is built to test Disulfide oil. The results of this simulation were compared to the results of using DSO in pilot to identify the deviation.

- *Experimental setup*

The P&ID (piping and instrumentation diagram) and the picture of Despoil used in this study is illustrated in fig.1 and fig.2respectively.

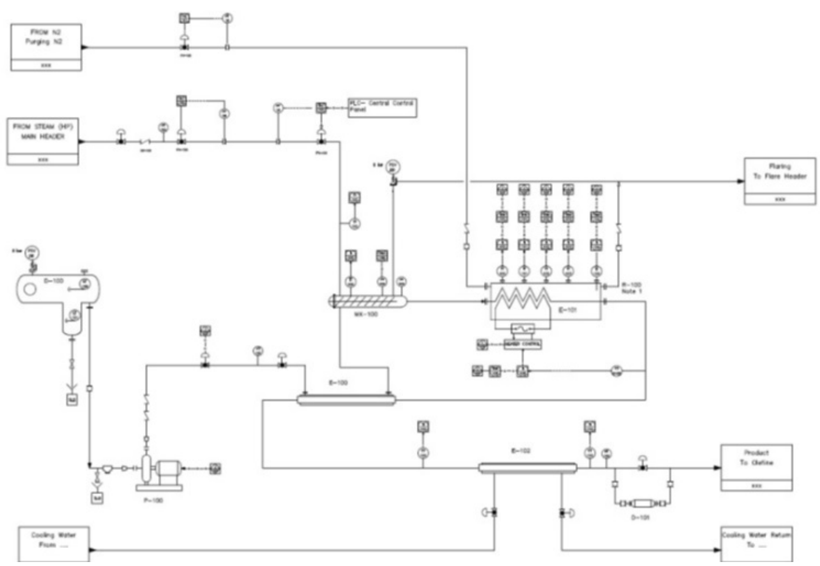

Fig. 1: P&ID generated for DSO pilot

Fig. 2: Experimental pilot built for simulation

Simulation

- *Simulation description*

Experimental data from the DSO Pilot were used as a basis to perform the process simulation using Aspen HYSYS. The DSO composition has kept at a ratio of 1:15by adjusting process conditions with injection of steam and the simulation enables to predict process conditions for the unit operations. In this simulation, the resulted Product composition indicated 0.0151, 0.0118, 0.9390 and 0.0341 mole fractions of H2S, CO2, H20 and Methane respectively that are listed in table 1, with a steam/DSO ratio of 15."F" stream moves to furnace. Therefore Gas stream from PIPE-100 in the simulation moves to the furnace (reactor) and a branch of it moves to sampling point to analysis the composition.

Table 1- Composition of stream inserted or calculated in model

Composition of stream(mole fraction)	DSO	Steam	F(Product)
Dimethyl-Disulfide	0.1038	0	0
Methyl-Ethyl-Sulfide	0.3932	0	0
Diethyl-Sulfide	0.4926	0	0
Hydrogen-Sulfide	0.002	0	0.0151
Carbon-Dioxide	0	0	0.0118
Water	0	1	0.9390
Methane	0.0001	0	0.0341
Ethane	0.0001	0	0
Propane	0.0001	0	0
Carbonyl-Sulfide	0.0011	0	0
Methyl-Mercaptan	0.0030	0	0
Ethyl-Mercaptan	0.0030	0	0
Carbon-Disulfide	0.0010	0	0

As seen in table 1 all the sulfur material in the DSO stream converts to H2S Completely

- *Assumptions*
  - ✓ DSO is injected at the 25 $^{\circ}C$ temperature under atmospheric pressure in system.
  - ✓ Steam is injected at 180 $^{\circ}C$ temperature and 10 bar pressure.
  - ✓ DSO stream after the pressure increasing will mixed with "steam2" in 5 bar.
  - ✓ Assuming pilot of DSO follows Gibbs Equilibrium, it is modeled with a Gibbs reactor in HYSYS,Named GBR-100

- ✓ The inlet steam is full of water in gas phase.
- ✓ The length of pipe to the furnace is about 30 M and the material often usedis mild steel.

- *Aspen HYSYS model and data of process*

The composition of DSO is determined byLaboratory of Amir kabirpetrochemical.Nomenclature andabbreviation Descriptionis given in table 2. As previously mentioned for the purpose of this research, DSO is stored at the 25 ℃ temperature under atmospheric pressure conditions in a special storage tank. In the pilot experiment, DSO was preheated up to a temperature of 800℃, and it was injected into the heat pipes.

Table 2- Nomenclature andabbreviation Descriptionin the simulation of process

Nomenclature	Description
Pump to increase DSO pressure	P-100
Throttling valve to decrease the pressure of steam	VLV-100
Mixture to blend of two stream	MIX-100
Gibbs reactor	G
The distance between pilot and furnace	PIPE-100
The furnace of olefin plant	Furnace
Abbreviations	Description
Disulfide OIL	DSO
Vapor of water	Steam
Mix of DSO and steam	SD
Process flow diagram	PFD

- *The Overall Schematic of Produced by ASPEN HYSYS*

The developed model, shown in Fig. 3, assumes the injection of DSO and steam into a Gibbs reactor after mixing two stream in MIX-100.The pipe size (24.31-33.41 mm ID) was selected in order to maintain the pipe stability under the current operating conditions and heat losses across the pipe enabling direct estimation of temperature and pressure gradients of injection and production. The length of pipe is 30 M. The produced gases are in F stream.

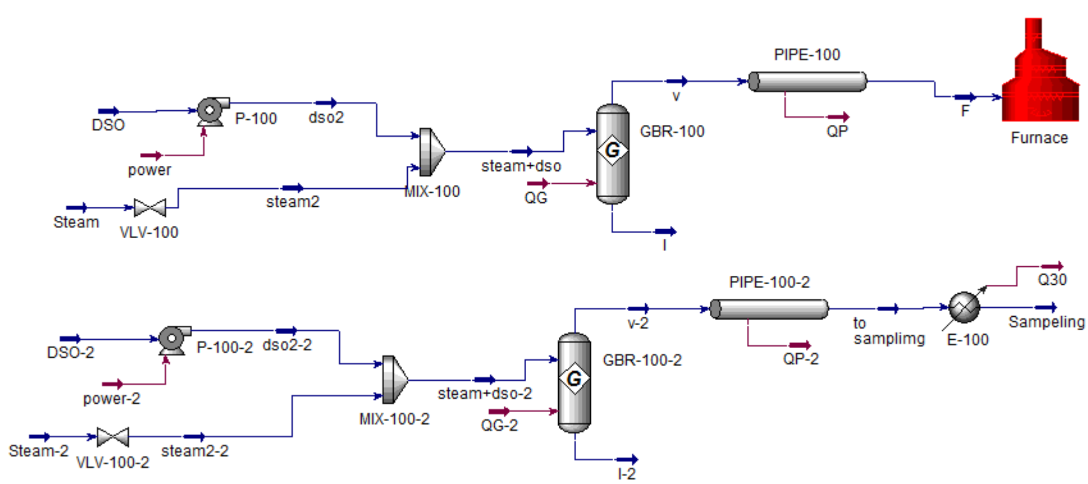

Fig. 3: ASPEN Hysys model of DSO Pilot for decomposing and sampling

The system parameters for inlet and outlet streams are given in table 3

Table 3. Simulation results

Parameter	DSO	Steam	SD	V	L	F
Molar flow (kgMole/hr.)	0.01194	0.8326	0.8446	0.8650	0	0.8650
Temperature(c)	25	180	153	800	800	422
Pressure(kpa)	100	999	500	500	500	499

Laboratory results of DSO test in pilot

- *GCCalculations for the Results of the DSO Test on the Pilot*

The following calculations indicated amount of the H2S from DSO injection

$$x = 100 * \frac{Y}{1.43}$$

X=Conversion of DSO to H2S
Y= Mole fraction of H2S calculated by GC

Fig. 4: AmirKabir petrochemical GC device (CP-SIL5CB, Varian 3800)

The following table indicated amount of the H2S from DSO calculated by GC.According to the calculations 99% conversion rate is gained.

Table 4. The calculations for the H2S gas produced from DSO

Time of DSO Injection (min)	30	60	90	120	150	180	210	240	270	300	330	360	390	420	450
Moles of H2S calculated by GC	0.78	0.84	0.90	1.04	1.14	1.28	1.39	1.39	1.42	1.42	1.42	1.42	1.42	1.42	1.42
Conversion of DSO to H2S (%)	54	58	63	72	79	88	96	97	99	99	99	99	99	99	99

- *Generated curve and equation for Laboratory results*

Figure and formula for this process is shown in fig.5,r^2 is 0.999627404 that means goodness of fit of model.

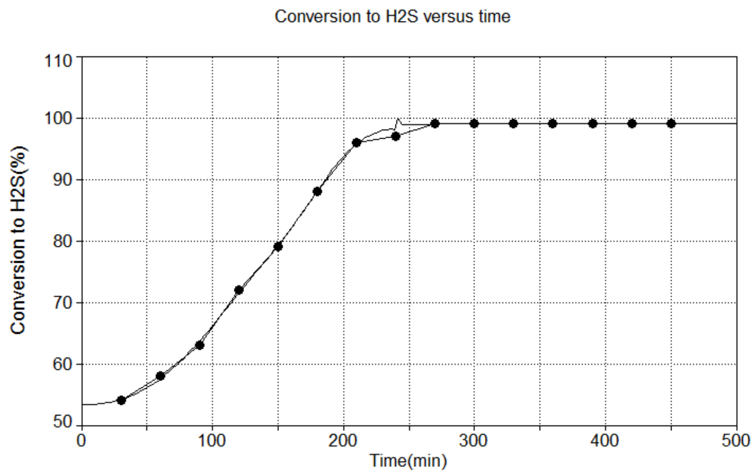

Fig. 5: Conversion of DSO to H2S

Gained equation for H2Sproduction after DSO injection is:

$$Y = \frac{\mathbf{a} + cx^2 + ex^4 + gx^6 + ix^8 + kx^{10}}{\mathbf{1} + bx^2 + dx^4 + fx^6 + hx^8 + jx^{10}}$$

And the equation coefficients are included as following:

a= 2839.9375, b = -3.3217016e-5, c = 0.002905863, d =1.9271003e-9, e = 1.3021933e-5, f = 1.0878021e-13, g = -1.0164299e-9, h =2.8515787e-18 i = 2.7747241e-14 j = -2.5281335e-23, k = -2.4747049e-19 and r^2 is 0.999627404

Results and Discussion

Comparison of Aspen HYSYS data and the results of GC for DSO injection indicated a fair enough approximation and revealed a few different in outlet stream composition. Conversion rate of H2S is given in table 5. By useof more time, the laboratory data results the better comparison with the simulation data.

Table 5- Comparison of simulation and laboratory results

Parameter	GC Test	Aspen HYSYS
Temperature(°C)	800	800
Pressure(bar)	4.93	5
H2S(Mole fraction)	1.42	1.51
H2S conversion rate (%)	99	99.99

Conclusions

In this paper Aspen HYSYS is used to set up a model for a DSO Pilotto predict the product composition and conversion rate. A piping and instrumentation diagram (P&ID) with various unit operations generated, the model is able to predict the outlet DSO composition and the simulation results are in good agreement with the experimental results Gained from GC calculations. Thus a model was successfully developed on Aspen HYSYS simulation for determining the sensitivity of parameters affecting the DSO injection process.

According to the calculations and simulations presented in this paper, DSO is a good alternative to produce H2S. Considering the fact that the DSO reactor was built, and the tests revealed that this pilot allows for complete replacement. By simulating the process, 99.99% hydrogen sulfide is gained (as calculated) and the other sulfur-containing materials, mercaptans, etc. do not remain in the production. In other hand this simulation indicates the 99.99% H2S conversion of DSO in outlet stream to furnace. The model is able to predict the conversion rate of sulfur material to H2S and the calculation from GC confirms it.Bycomparingthe model results with calculated data from GC in the same condition, it is concluded that the developed model is reasonably accurate and can be used for analysis.

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