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Simulation of Hydrodesulfurization (HDS) Thiophene in Naphtha over a Cobalt - Molybdenum Catalyst

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Abstract: ***The target of this paper is to simulate one of the main important treatment processes used in petroleum refinery, this process is the hydrodesulfurization (HDS) of naphtha. HDS is accomplished by converting sulfur compounds contained in naphtha to hydrogen sulfide (H_2S); this is then removed as a gas by stripping. Generally, HDS used to reduce environmental pollution caused by sulfur dioxide (SO_2) emission that result from various combustion practices and for pretreatment of catalytic reformer feeds to prevent sulfur poisoning of the catalysts. Cobalt–molybdenum on alumina supported ($CoMo/Al_2O_3$) is used as a catalyst. There are a wide range of models used to simulate HDS of naphtha. Three models have been chosen to simulate the process. These models were applied on three different types of Libyan crude, which are Es–Sider, Brega, and Hamada crude. A computer program used to simulate the models for HDS process. The results shows that all models gives the conversion of thiophene to be greater than 90%. That means the HDS product contains as maximum as 5 ppm of sulfur which is suitable to be feedstock for catalytic reforming process. Model 1 gives the best prediction of HDS reactor performance for specified operating conditions (temperature and pressure).***

Keywords: petroleum refinery, Hydrodesulfurization, catalyst, kinetic reaction

1. Introduction

Recently, interest in obtaining low–sulfur fuels has increased as a result of stringent environmental regulations for emissions of sulfur dioxide into the atmosphere [1]. However, for the environmental reasons, the maximum allowable content must not be more than 0.3% [2]. Another important reason for removing sulfur from naphtha streams within a petroleum refinery that sulfur, even extremely low concentration, poisons the noble metal of the catalyst in catalytic reforming unit that are subsequently used to upgrade the of the naphtha streams [3]. To date, HDS technique is one of the best methods used to remove sulfur compounds from naphtha stream, because of its high efficiency and low environmental pollution [1].

HDS is a catalytic process where reactions take place in a fixed–bed reactor at elevated temperatures ranging from 300 to 400°C and elevated pressures ranging from 30 to 130 atmosphere of absolute pressure [3], typically in the presence of a catalyst (often $CoMo/Al_2O_3$ cobalt molybdenum–on alumina base) [4] because, it has proven to be high selective, easy to regenerate and highly resistance to poisons [5]. The figure below is a schematic diagram of the HDS unit.

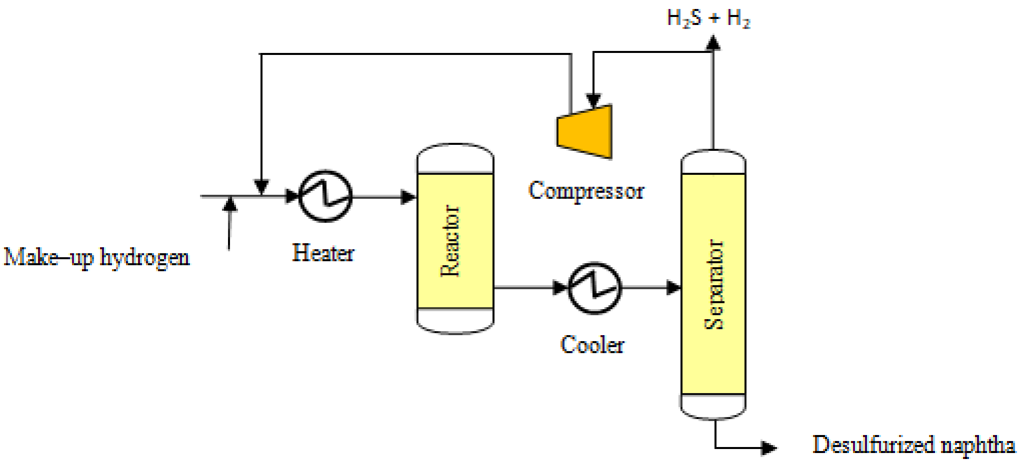

Figure 1: HDS process diagram

2. Naphtha HDS

Naphtha is a fraction of crude oil, usually consists of 15–30% by weight of crude oil and boils between 30 and 200°C. This fraction contains some impurities such as sulfur, oxygen and nitrogen compounds [6]. The typical classes of sulfur bearing compounds present in naphtha are illustrated in the table 1. In HDS, thiophenes and benzothiophenes are the least reactive molecules (usually thiophene, 15–30 times slower than the rate for other compounds) [5]. Thiophene desulfurization is assumed to be rate controlling and is therefore used to represent the kinetics of naphtha desulfurization [7].

Table 1: Classification of sulfur compounds in naphtha

Compound	Structure	Boiling point	Reactivity
Mercaptans	R – SH		Rapid
Sulfides	R – S – R		Moderate
Thiophene	C_4H_4S	84°C	Very slow
Benzothiophenes	C_8H_6S	221°C	Slow

The thiophene reaction is;

$$C_4H_4S \;+\; 3H_2 \;\longrightarrow\; C_4H_8 \;+\; H_2S$$

3. Reaction Kinetics

The reaction of thiophene with hydrogen was classified as a heterogeneous catalytic reaction. It is necessarily involve chemical and physical interaction between the gas mixture (thiophene and hydrogen) and solid catalyst $CoMo/Al_2O_3$. At least one of the reactant components will be chemisorbed by the catalyst and then transformed into a chemisorbed product at the catalyst surface. Transport of reactants and products occurs both in interior porous structure of the catalyst and exterior to the catalyst particles. A conceptual model of the catalytic process has been formulated for chemical reactor in which the overall process occurs is adequately, each of these chemical and physical process can be expressed mathematically and coupled together to provide a complete description (models) of the catalytic system [8]. These models can be used for design and prediction purposes. Models used to describe HDS of thiophene are expressed by Langmuir–Hinshelwood model. The basis of this model is that each of reacting components is initially chemisorbed at the catalyst surface before rearrangement on the surface and subsequent desorption of the products [9]. Thiophene HDS over $CoMo/Al_2O_3$ was first order in thiophene and hydrogen and appreciably inhibited by thiophene, hydrogen, and hydrogen sulfide. Table 2 illustrate three different models for the HDS of thiophene as a function of partial pressure [10].

Table 2: Kinetic model used in the HDS of thiophene

Model No.	Rate Equation
1	$r_T = \frac{kP_TP_H}{(1 + K_TP_T + K_{H_2S}K_{H_2S})}\left(\frac{1}{1 + K_HP_H} + k''\right) \rightarrow (10)$
2	$r_T = \frac{kP_TP_H}{(1 + K_TP_T + K_{H_2S}K_{H_2S})^2} \quad \rightarrow (11)$
3	$r_T = \frac{kP_TP_H}{(1 + K_TP_T + K_{H_2S}K_{H_2S})^2} \quad \rightarrow (11)$

The parameters of these models are calculated by using Arrhenius equation:

$$K = K_0 \exp\left(\frac{-E}{RT}\right) \qquad \rightarrow (1)$$

The parameters for the models are listed in table 3.

Table 3: Models parameters.

	Model 1	Model 2	Model 3
k	2.02768×10^{-6} $\mathrm{kmol.kg^{-1}.s^{-1}.Torr^{-2}}$	8.196×10^{-3} $\mathrm{kmol.kg^{-1}.s^{-1}.Torr^{-2}}$	2.02768×10^{-6} $\mathrm{kmol.kg^{-1}.s^{-1}.Pa^{-2}}$
k"	4.6193×10^{-9} $\mathrm{kmol.kg^{-1}.s^{-1}.Torr^{-2}}$		
K_T	$5.821 \times 10^{-8}\ \mathrm{Torr^{-1}}$		
K_S			
K_H			

The global rate of reaction which includes interparticle diffusion is given as:

$$r_P = \eta\, r_T \qquad \rightarrow (2)$$

The detail equations used to compute the global rate of reaction from the surface reaction rate are summarized in table 4 [12].

Table 4: Equations used for calculating effectiveness factor

$$D_{AB} = \frac{0.04381T^{1.5}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P\sigma_{AB}\Omega_D} \qquad \rightarrow (1)$$

$$D_{KA} = 97\,r\left(\frac{T}{M_A}\right)^{1/2} \qquad \rightarrow (2)$$

$$D = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_{KA}}} \qquad \rightarrow (3)$$

$$\delta = \frac{1}{\varepsilon} \qquad \rightarrow (4)$$

$$D_e = \frac{\varepsilon D}{\delta} \rightarrow (5)$$

$$\phi_c = \frac{r_s}{3}\sqrt{\frac{k\rho_b}{D_e}} \rightarrow (6)$$

$$\eta = \frac{1}{\phi_c}\left(\frac{1}{\tanh 3\phi_c} - \frac{1}{3\phi_c}\right) \rightarrow (7)$$

4. HDS Reactor Model

An isothermal plug flow model was used as the basic equation for the HDS reactor, namely:

$$\frac{W}{F} = \int \frac{dX}{r_p} \rightarrow (3)$$

This equation coupled be re–write as:

$$\frac{dX}{d\left(\frac{W}{F}\right)} = r_p \rightarrow (4)$$

Equation 4 is a first order ordinary differential equation. This equation could be solved numerically to find the value of conversion X by using a computer program (Rung–Kutta method) and the value of (W/F) is computed directly by using Trapezoidal rule.

In this study, the three feed streams of Sidra, Brega, and Hamada crudes were analyzed separately by using three different models of show which model will give the best results for the weight of catalyst by comparing these results with the actual amount of the catalyst used for the HDS process in Zawia refinery. Note that, the outlet stream from HDS unit should contain as a maximum of 5 ppm of sulfur. The characterization of the naphtha feed and reactor conditions were summarized in table 5.

Table 5: Feedstock properties and HDS reactor conditions

Naphtha charge, m^3/hr	55
Feed sulfur content, ppm:	
Sidra crude	350
Brega crude	240
Hamada crude	170
Specific gravity @ 15°C	0.714
Density, kg/m^3	33.992
Boiling point range, °C	35 – 165
Molecular weight, kg/kmol	108.4
Hydrogen to hydrocarbon ratio	6
Reactor inlet temperature, °C	320
Reactor outlet temperature, °C	319
Reactor inlet pressure, kg/cm^2	29.5
Reactor outlet pressure, kg/cm^2	29
Hydrogen rich gas:	
Rate, m^3/hr	40309.0483
Percent H_2	76

5. Results and Discussion

The results shows that all models give the conversion of thiophene to be greater than 90%. This means that HDS products contains as maximum as 5 ppm of sulfur which is suitable to be a feedstock for catalytic reforming process. The conversion of sulfur components (thiophene) contained in Hamada crude is greater than conversion of sulfur components contained in Brega and Sidra crudes by using the same model, which means that as the naphtha contains less sulfur as the process becomes more efficiently. The amount of catalyst was calculated for each model using Trapezoidal rule. The catalyst used is $CoMo/Al_2O_3$ and the actual amount of catalyst was 4061.28 kg. by comparing this value with the calculated value, it's clear that model 1 gives the most accurate value for the weight of catalyst used for accomplished HDS process which is equal to 4061.53 kg for Hamada crude. The weight of catalyst needed for hydrodesulfurized Brega and Sidra crude were found to be 4063.57 and 4065.24 kg, respectively. The error was found to be less than 1% while the error in other models was found to be greater than 10% which means that these models cannot be applied for this process. Therefore, it was found that model 1 gave the best prediction of HDS reactor performance for a specific operating conditions (i. e., temperature and pressure). The results are tabulated as follows:

Table 5 (a): Es–Sider crude

Model No.	Sidra Crude			
	ϕ	η	X	W (kg)
1	2.207	0.385	0.996	4065.33
2	1.395	0.545	0.980	4123.00
3	1.000	0.670	0.903	4201.25

Table 5 (b): Brega crude

Model No.	Brega Crude			
	ϕ	η	X	W (kg)
1	2.207	0.385	0.997	4063.75
2	1.395	0.545	0.972	4114.36
3	1.000	0.670	0.900	4150.15

Table 5 (c): Es–Sider crude

Model No.	Hamada Crude			
	ϕ	η	X	W (kg)
1	2.207	0.385	0.998	4061.53
2	1.395	0.545	0.962	4112.00
3	1.000	0.670	0.899	4137.39

The effect of thiophene pressure o the rate of HDS was shown in figure 1 for the three crudes, this was through model 1. The rate increased linearly with thiophene pressure. By comparing the result, it was found that the effect was the highest for the Sidra crude (fig. 2a) after that Brega crude (fig. 2b) ad Hamada crude (fig. 2c), respectively. Also, as shown in figure 3 for the crudes, thiophene rates decreased with increasing conversion percent.

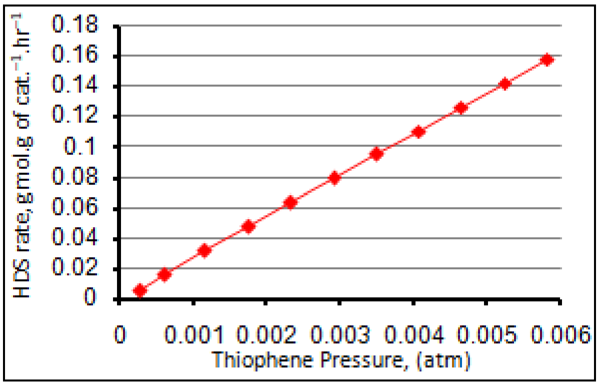

Figure 2 (a): Effect of thiophene pressure on the reaction rate, Sidra crude

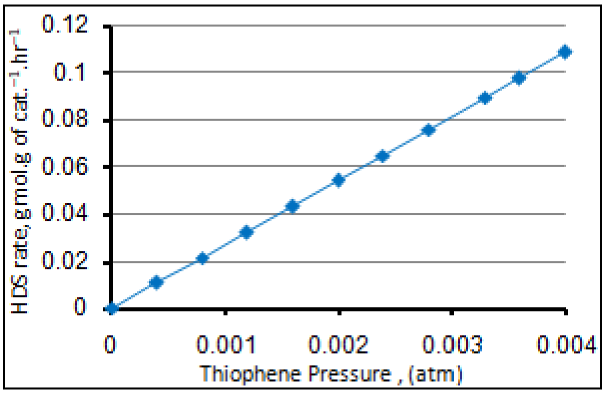

Figure 2 (b): Effect of thiophene pressure on the reaction rate, Brega crude

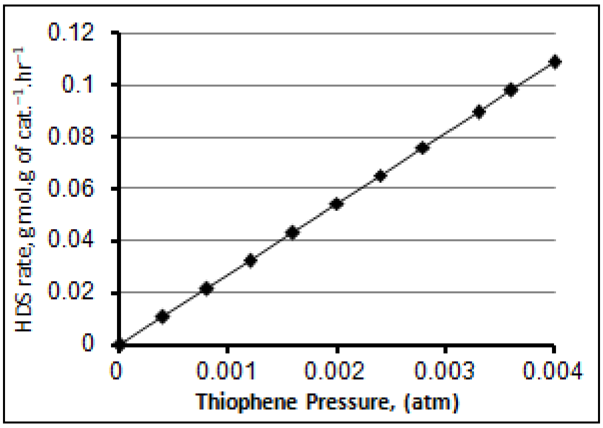

Figure 2 (C): Effect of thiophene pressure on the reaction rate, Hamada crude

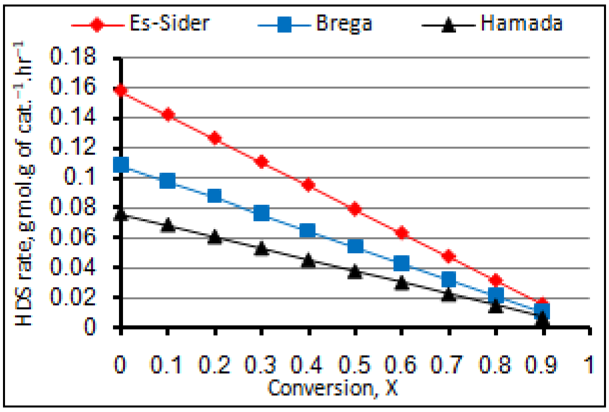

Figure 3: Effect of conversion on the reaction rate, Hamada crude

Nomenclature

D	combined diffusivity, ft^2/hr
D_{AB}	bulk diffusivity, ft^2/hr
D_e	effective diffusivity, ft^2/hr
D_K	Knudsen diffusivity, ft^2/hr
E	activation energy, J.kgmol^{-1}
F	feed rate, lmol.hr^{-1}
k_i	reaction rate constant of species i.
K	adsorption equilibrium constant of species i.
p_i	partial pressure of species i, atm
P	total pressure, psia
r_i	rate of disappearance of species i due to reaction, lbmol.lb of catalyst^{-1}.hr^{-1}
r_p	global reaction rate, lbmol.lb of catalyst^{-1}.hr^{-1}
r_s	radius of pellet, ft
r_T	thiophene rate, lbmol.lb of catalyst^{-1}.hr^{-1}
R	gas constant, 10.73 psia.ft^3.lbmol^{-1}.R^{-1}
T	absolute temperature, K
W	mass of catalyst, lb
X	conversion

Subscripts

A	component A
B	component B
H_2	hydrogen
H_2S	hydrogen sulfide
i	component i
t	total
T	thiophene

Greek letters

ε	void fraction
η	effectiveness factor
ρ	density, kg.m^{-3}
ϕ_c	Thiele modulus for porous catalyst
δ	tortuosity factor
σ	average collision
Ω	temperature–dependent collision integral

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