Kinetic Parameter Estimation For Hydrodesulphurization Of Gas Condensate On Cobalt-Molybdenum Catalysts

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Abstract—**The main objective of this study was to obtain the influence of some reaction parameters on hydrodesulphurization of Iranian gas condensate that has been reported in the article. In order to obtain a suitable model that can lead to behaviour prediction of this process. Reaction kinetics of hydrodesulphurization of gas condensate in trickle bed reactor by using Cobalt-Molybdenum (Co-Mo / Ɣ-AL$_2$O$_3$) catalyst and also the role of various factors such as temperature and space velocity has been investigated. To obtain constant reaction rate Arrhenius equation has been used and temperature range is between 563-593 K (290-320 °C) and space velocity 1 h^{-1} is considered. Reference substance sulfur is thiophene and reaction kinetics are assumed to be exponential model. The results indicated that the degree of reaction of sulfur with reference to the assumed *n*=1.4 is more consistent with experimental data. The activation energy of the reaction in this case is equal to 79.63 KJ/Mol and the Arrhenius constant equal to 2.8*10^8 that graph of Lnk versus 1/T is a straight line with –E/R slope.About the space velocity we see that at temperatures of 563 K (290 °C) and 593 K (320 °C) the following results were obtained in this way that by increasing the space velocity, conversion of sulfur compounds decreases. Increased space velocity produced the opposite effect. These results and the change of either one or more process parameters or of the catalyst type enabled performance of the industrial reactor.**

Keywords—hydrodesulphurization, cobalt-molybdenum catalyst, trickle-bed reactor, gas condensate

I. INTRODUCTION

The hydrodesulphurization process of hydrogen on petroleum products have now widely performed across the world. The crude oil contains some compounds such as sulfur, nitrogen, oxygen, metals and unsaturated compounds that cause environmental pollution and corrosion of equipment and deactivation of catalyst. The sulfur content of crude oil is one of the factors that have the greatest role in the prices of crude oil. The aim of Hydrotreating operations is eliminating or reducing these harmful species. If the desired operation merely involves the removal of sulfur compounds using a hydrogen process called Hydrodesulphurization. There are many different forms of sulfur in crude oil that are including the mercaptan (*R-SH*) ,disulfide (*R-S-S-R*), poly-sulfides (*R-S$_n$-R*), thiophene ,benzothiophene, and other derivatives alkyl.

Commonly catalyst that is used in the refining with hydrogen, oxides or metal sulfides such as cobalt, nickel, iron, molybdenum and Tungstenthat are on alumina basic. Adding neutralize particles to the catalyst can enhance catalyst wetting coefficient and also work efficiency [1].

Hydrodesulphurization reactions in general are as follows [2]:

$$organic\ sulur\ compound + H_2 \rightarrow H_2S + desulfurized\ organic\ compound \qquad (1)$$
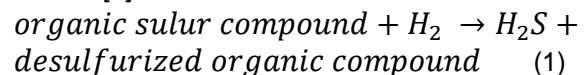
The mass transfer resistance of the catalysts can be divided into two categories: pitting resistance and film resistance.Catalyst pore resistance against the entrance and exit of products from reactants to show the hole resistance. However, the film resistance is the resistance of the gas film surrounding the catalyst to the entrance and exit of reactants and products [3]. Hydrotreating catalyst is substance with high especial area that contains the active compound and an accelerator that they are also based on a uniform distribution. Usually, catalysts based on gamma-alumina basic, which in some cases small amounts of silica or phosphorus can be added to create a material with a high surface area and porous structure. Cobalt-molybdenum catalyst used for the ratio less than 100-500 ppm of sulfur with a low pressure condition that they show better performance rather than nickel-molybdenum catalysts (*Ni-MO Cat*). In general,the catalyst for the large-scale of hydrodesulphurization can be used. Hydrodesulphurization catalysts generally consist of monolayer coverage and uniform distribution of oxides of metals such as molybdenum and oxides of group *VIB* and group *VIII* metals such as cobalt catalyst based on gamma-alumina. In trickle

bed reactors, gas and liquid flow down the side of the fixed bed catalyst, and there is a drop in the liquid phase and the gas phase is continuous [4]. Having made in the design of the reactor, the reaction is considered to the lowest rate of reaction.This is due to the slow reaction that will consume the most chemical potential. Thiophene and its derivatives have the lowest rate of the condensate and its use provide possibility to model the real feed.One way to get a degree of hydrodesulphurization reaction rate equation determined using experimental data and Arrheniusequation parameters.In this study the rate equation as an exponential equation of degree n, was initially supposed to be as follows.

$$-rate = \frac{dC}{dt} = KC^n \qquad (2)$$

In equation (2), C is the concentration of sulfur reference material, n stands for the degree of reaction, t is the time and K is kinetic parameter. For equation 2 the case that the degree of reaction is the opposite of ($n \neq 1$) the equation the following form

$$\frac{1}{n-1}\left[\frac{1}{C_p^{n-1}} - \frac{1}{C_f^{n-1}}\right] = \frac{K}{LHSV} \qquad (3)$$

In equation 3, C_f stands for sulfur concentration in the feed used, C_p stands for the remained sulfur concentration in the product, and $LHSV$ (h^{-1}) is liquid space velocity.Arrhenius form is used for calculating the constant reaction kinetics. The k_0 isconstant of Arrhenius equation, E is the activation energy (KJ/Mol), T is temperature (K) and R is the gas constant is (KJ/Mol.K). Arrhenius equation parameters that must be determined are the activation energy and Arrhenius constant.

$$k_{HDS} = k_0 \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

II.   RESULT

Therefore, hydrodesulphurization reaction was at temperatures between 563 to 593 K (290 to 320 ˚C) and for the same $LHSV$=1 (h^{-1}). According to the curves shown in Figure 1, that Ln (K) versus 1/T is plotted, the activation energy and Arrhenius constant is given by the figure [1], the slope of the line equals by the ratio (-E/R) and intercept equal to Ln (k_0). The Calculated value of the activation energy is E=79.63 KJ/mol and k_0 is approximately equal to $k_0 = 2.8*10^8$. The activation energy for the reaction in several studies that these differences would be due to the difference between the type of feed, the sulfur source, the type of catalyst used,
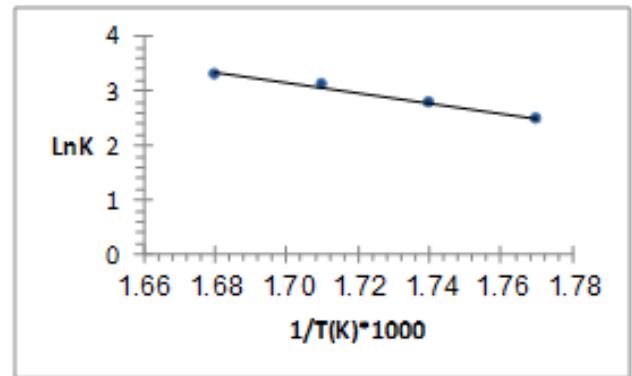reaction mechanisms and interface physical phenomena of the phases [5].

Fig1- Arrhenius parameters

To determine the reaction kinetics, operating parameters such as temperature, space velocity change and its effects were studied.The reactor is assumed to be isothermal. To determine the response rate of the experimental data in Table 1 is used and obtain the degree of reaction, so that the left term of equation (3) were plotted according 1/LHSV The resulting graph is a straight line and at a level that is the most consistent with experimental data the researchers consider it as the degree of reaction. In this study, calculations are based on five degrees 1.2, 1.3, 1.35, 1.4, and 1.5that they are shown respectively in figures 2,3,4, 5and 6 that maximum compatibility is obtained for n = 1.4.
Result of curves for different degrees is mentioned below and the reaction degree for n= 1.4 has the best match. Some further researches in this area are such as studies done by Yui and Ng [6] and Yui and Sanfond[7].
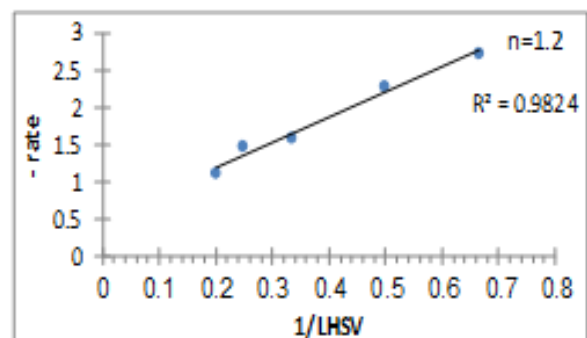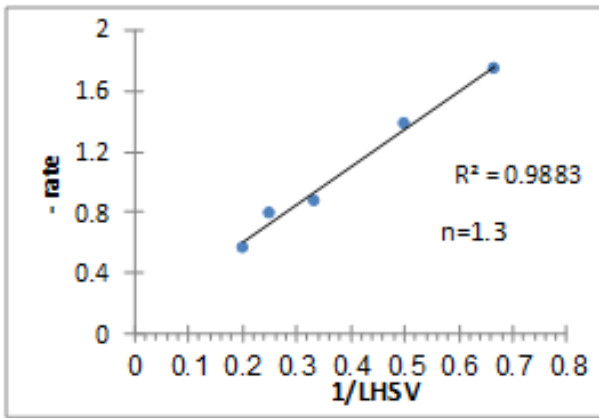

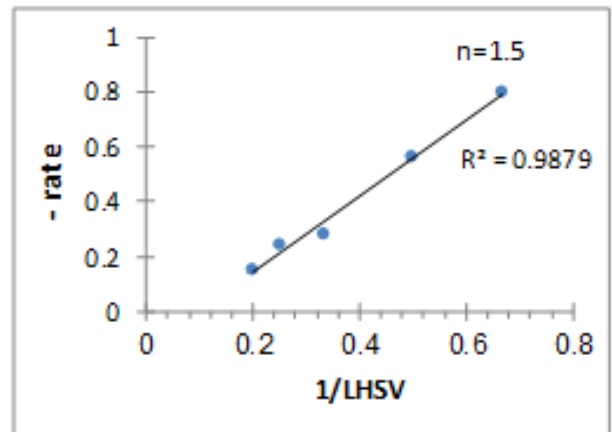**Fig 2-**For the degree n=1.2

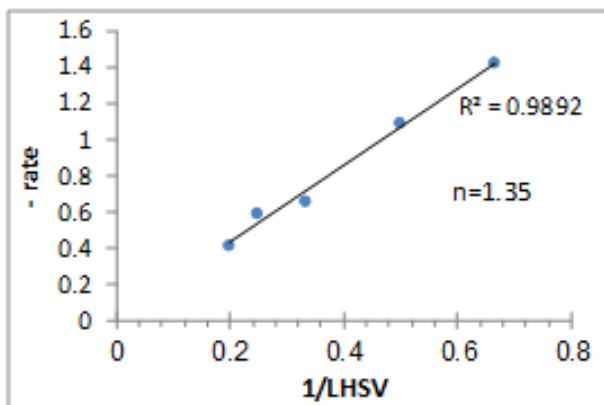**Fig 3-**For the degree n=1.3

Fig 4- For the degree n=1.35

Table 1. Experimental data to determine the degree of reaction			
T(°C)	T(K)	LHSV(h⁻¹)	C_p(ppm)
290	563	1	318
300	573	1	196
310	583	1	113
320	593	1	56

Fig 5- For the degree n=1.4

Fig 6- For the degree n=1.5

The liquid space velocity on conversion of compounds as the last parameter is examined at two temperatures 563 K (290 °C) and 593K (320 °C).The obtained results indicated that the conversion rate decreased with increasing space velocity of fluid. This is because it would be caused by the increasing space velocity molecules feed missed their interaction through the active site of the catalyst. The results are presented in figures 7 and 8.

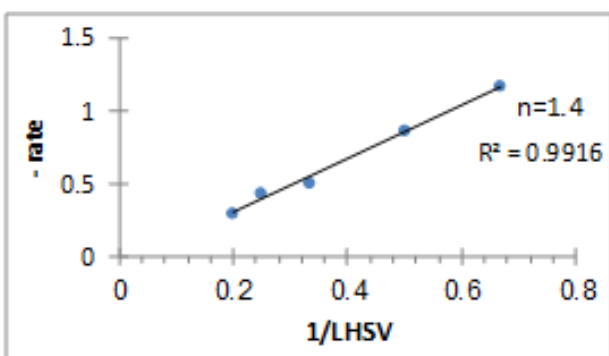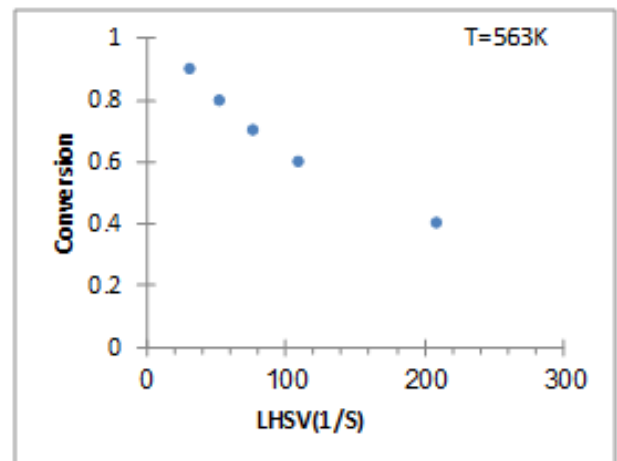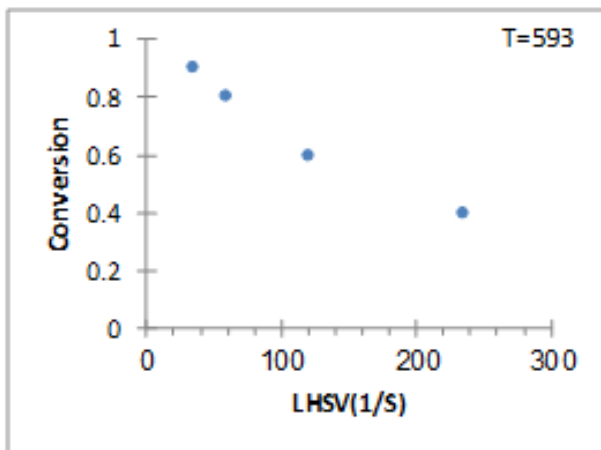| Table 2.Feedstock properties.	
Boiling range (K)	288-623
Sulfur (%wt)	0.22
Nitrogen content (ppm)	16
Aromatic (% vol)	16
Specific gravity	0.756

Fig 7- The role of space velocity on the conversion rate at 563K

Fig 8- The role of space velocity on the conversion rate at 593 K

III.   CONCLUSION

Hydrodesulphurization reaction kinetics of hydrogen gas condensate using cobalt-molybdenum catalyst was investigated in this study. Thiophene sulfur was used as reference substance. Because the investigation is to show that merccaptans, sulfides and polysulfide readily lose their sulfur atoms while thiophene,

and its derivatives have the least tendency to lose their sulfur atoms. Using the experimental data can be used to model the degree of reaction that determined to be 1.4, the most consistent with experimental data. Kinetic constants equal to the activation energy $E =$ 79.63 (KJ/mol) and constant of Arrhenius equation is $k_0 = 2.8*10^8$. The result of the research carried out and compared with the other papers results in journals implies that the model is efficient and also able to predict its process.

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