

# THE EFFECT OF MASS TRANSFER RESISTANCE ON THE KINETICS OF THIOPHENE HYDRODESULFURIZATION

K. Ghanbari\*, M. Mohammadi and M. Tajerian

*Research Institute of Petroleum Industry – Tehran – Iran – P.O. Box 18745-4163 Phone: +98(21) 5901021-51 (Ext. 4190) Fax: +98 (21) 5931440, e-mail: Ghanbarik@yahoo.com*

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## Abstract

In kinetic study of catalytic reactions, due to mass transfer rate can be effective in adding to chemical kinetic, so it is necessary to study these effects firstly. The present work investigates the hydrodesulfurization of gas condensate, to determine the effect of interface mass transfer resistance. The entire work was performed in a hydrodesulfurization (HDS) pilot plant unit, located in Research Institute of Petroleum Industry (RIPI). For the tests, a commercial HDS catalyst (CoMo) was used and the feed (gas condensate) provided by South Pars gas field of Iran. The objective of the work was to investigate effect of mass transfer limitations in catalytic reaction of thiophene HDS. It was verified that mass transfer resistance has not a significant effect on the reaction rate. The results are presented as graphs and tables.

**Keywords:** *kinetic; thiophene; hydrodesulfurization; mass transfer resistance; catalyst*

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## 1. Introduction

In these years, demand for high quality fuel has grown significantly. In order to meet this increased demand, the refineries use HDS units to remove sulfur compounds from fuels. Desulfurization is one of the important processes in refinery plants. Most usual method for deep sulfur removal from petroleum cuts is hydrodesulfurization (HDS). Thiophenic components are known to be the most refractory organic sulfur-containing components. Rigorous kinetics for the hydrodesulfurization (HDS) of thiophene has already been derived (Van Parys and Froment<sup>[8]</sup>).

For thiophene, hydrodesulfurization rate equation has been reported by Hensen<sup>[7]</sup>, while most of them did not determine the influence of the mass transfer resistance, exactly. Furthermore, mass transfer limitation can be divided into two distinct phenomena.

The first mass transfer resistance is pore diffusional limitation, which is defined as the resistance of catalyst pores against reactants entrance and products exit. Another mass transfer limitation is film diffusional limitation, which is defined as the resistance of the gas film around the catalyst, against passing the reactants and products.

Three characteristics of catalyst, that effect on mass transfer properties of a typical catalyst are:

- The specific surface area of the support
- The dispersion rate of the active agents on the support
- The pore distribution of the support

These parameters, if they are satisfactory, tend to limit diffusional phenomena by facilitating the access of reactants and departure of products.

## 2. Experiments and Results

In this study, a set of experiments was performed to investigate the effect of interface mass transfer limitations on hydrodesulfurization reaction of gas condensate feedstock. For this purpose two phenomena of pore diffusional limitation and film diffusional limitation have been studied separately.

For kinetic study of HDS reaction, it is required that existing sulfur in the feed be only one type of sulfur compounds. So, gas-condensate from South Pars, which its specification is given in table (1), should become free from sulfur and then thiophene, , as the reference sulfur compound, is added to it for making a certain concentration of sulfur in feed.

In addition to feed preparation, the catalyst should be presulfided before using it with actual feed. Presulfiding of catalyst is done by dimethyl disulfide (DMDS), which is added to the Isomax gas oil, and circulated through the reactor bed.

**Table 1.** HDS feedstock properties

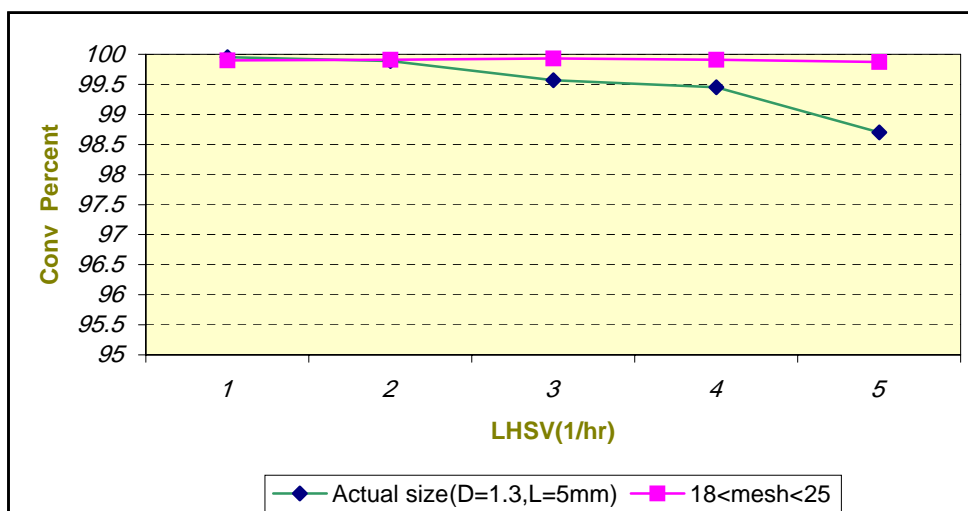
Type	Gas Condensate
Density, g cm <sup>-3</sup>	0.7561
Sulfur Content, %wt	0.22
Aromatic Content, %vol	16.0
Pour Point (°C)	-32
Viscosity, cst (20°C)	1.04
ASTM D-86 (°C)	IBP:15, 9%:36.5, 50%:150, 80%:250, 95%:350, FBP:350+

**Table 2.** Catalyst Properties (KF 757)

Surface area (m <sup>2</sup> /gr)	255
Pore volume (cc/100gr)	54
Cobalt (wt%)	3,15
Molybdenum (wt%)	12,5
Al <sub>2</sub> O <sub>3</sub> (wt%)	84,65

The physical and chemical properties of commercial catalyst KF 757 of Akzo Nobel company which is used in this study, have mentioned in table (2).

For investigation of pore diffusional limitation, firstly the commercial catalyst with real dimensions (D=1.3 mm, L= 5mm) in a microreactor has been used. In this set the conversion of reaction was measured with various feed flow and different feed to catalyst ratio (LHSV). Then catalyst was broken to very small particles, and previous tests were repeated by using this mesh size of catalysts (18<mesh<25), in the same microreactor. In this set of experiments, the conversion of HDS reaction was measured with the same amounts of feed flow and LHSV ratio.



**Fig 1.** The effect of pore diffusional limitation.

The results of these series of tests have been summarized in figure (1). With comparison of two curves, it is observed that in spite of reducing catalysts particle size to very small size, the conversion of reaction has not changed significantly. So it can be found that mass transfer resistant spring from pore diffusion has not any effect on the reaction kinetic.

For investigation of film diffusional limitation, some test was performed in the pilot scale reactor. In these tests, flow of feed passing through catalyst bed was changed to vary the amount of fluid velocity or in the other word to change the LHSV, and conversion of HDS reaction in any set points was measured.

The results of these two sets of tests have been illustrated in figure (2). It is seen that even the velocity of fluid increase to five times, the conversion of HDS reaction has not vary significantly. Therefore it is verified that mass transfer resistant spring from film diffusion has not any role in the reaction.

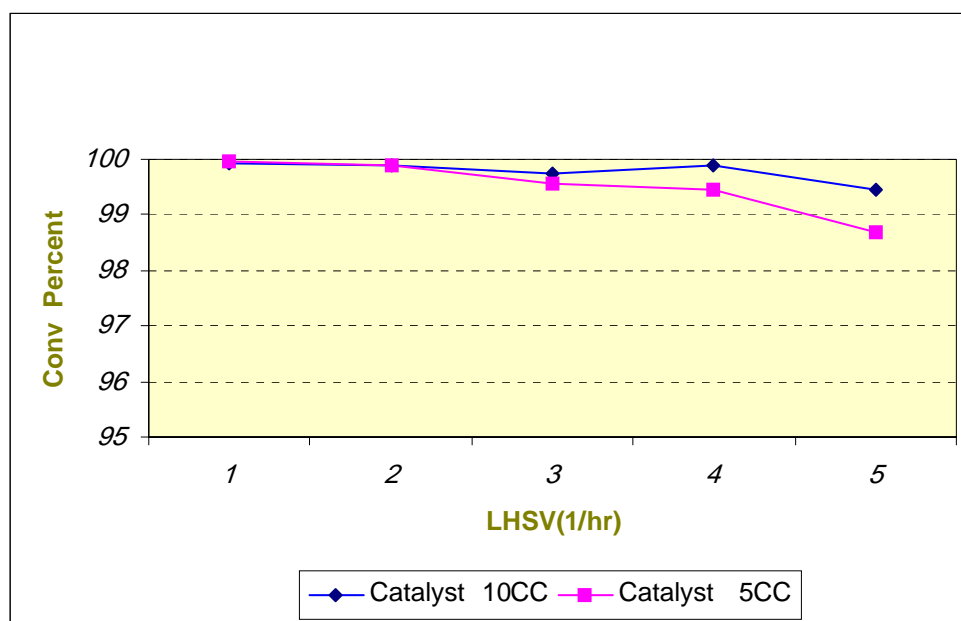


Fig 2. The effect of film diffusional limitation

Table 3. Results of mass transfer experiments

Catalyst Dimension	Sample No.	Operating Condition (H <sub>2</sub> /OIL=125, T=340°C, P=40bar)				Product Total Sulfur (ppm)
		LHSV	Catalyst (cc) (gr)		Q <sub>H<sub>2</sub></sub> (lit)	
5mmx1.3(D)mm	M1	3	10	9.04	4.6	26
5mmx1.3(D)mm	M2	4	10	9.04	6.2	10
5mmx1.3(D)mm	M3	5	10	9.04	7.8	57
5mmx1.3(D)mm	M4	2	10	9.04	3.1	12
5mmx1.3(D)mm	M5	1.5	10	9.04	2.3	7
5mmx1.3(D)mm	M6	1.5	5	4.21	1.2	5
5mmx1.3(D)mm	M7	2	5	4.21	1.6	11
5mmx1.3(D)mm	M8	3	5	4.21	2.3	44
5mmx1.3(D)mm	M9	4	5	4.21	3.1	57
5mmx1.3(D)mm	M10	5	5	4.21	3.9	134
18<mesh<25	M11	1.5	5	4.1	1.2	10
18<mesh<25	M12	2	5	4.1	1.6	9
18<mesh<25	M13	3	5	4.1	2.3	7
18<mesh<25	M14	4	5	4.1	3.1	9
18<mesh<25	M15	5	5	4.1	3.9	13

### 3. Conclusion

In this study performance of a commercial HDS catalyst (KF 757) was investigated. For this purpose the effect of interface mass transfer resistance was evaluated. Pore diffusional limitation was studied by comparisons of reaction conversion obtained from actual size catalysts and 18-25 mesh catalysts. It is verified that pore diffusion by comparison of conversions rate. Furthermore, film diffusional limitation was investigated by comparison of conversions from some fluid velocity passing through the reactor. It is proved that film diffusion has not effect on the reaction rate.

### References

- [1] Leo Alvarado Perea, "The effect of solvent on the kinetics and mass transfer resistance for 4,6 DMDBT HDS", *Int. J. Chem. React. Eng.*, 2005, 3, A 27
- [2] Hiroshi Yamada and Shigeo Goto, "Advantages of counter-current operation for Hydrodesulfurization in trickle bed reactors", *Korean J. Chem. Eng.*, 2004, 21(4), 773-776
- [3] Yao Wang, "Kinetics of Hydrodesulfurization of Dibenzothiophene catalyzed by sulfided Co-Mo/MCM-41", *Ind. Eng. Chem. Res.*, 2004, 43, 2324-2329
- [4] A. Marafi, "A comparative study of the effect of catalyst type on Hydrotreating kinetic of Kuwaiti atmospheric residue", *Energy & Fuels*, 2003,17, 661-668
- [5] Petr Steiner and Edd A. Blekkan, "Catalytic Hydrodesulfurization of a light gas oil over a NiMo catalyst: kinetics of selected sulfur components", *Fuel Processing Technology*, 2002,79(1), 1-12
- [6] A. Borgna, E. J. M. Hensen, J. A. R. van Veen and J. W. Niemantsverdriet, "Intrinsic kinetics of thiophene hydrodesulfurization on a sulfided NiMo/SiO<sub>2</sub> planar model catalyst", *Journal of Catalysis*, 2004, 221(2), 541-548
- [7] Hensen E.J.M. , Vissenberg M.J. , Beer V.H.J. de, Veen J.A.R. van, Santen R.A. van, *Kinetics and mechanism of thiophene hydrodesulfurization over carbon supported transition metal sulfides*, *J. Catal.* ,1996, 163, 429
- [8] Van Parijs, I.A., and G.F. Froment. "Kinetics of Hydrodesulfurization on a CoMo/ -Al<sub>2</sub>O<sub>3</sub> Catalyst" - I: "Kinetics of the Hydrogenolysis of Benzo-Thiophene." *Ind. Eng. Chem. Prod. Res. Dev.* Vol.,1986, 25, 431-436