HYDRODESULFURIZATION OF THIOPHENE OVER CO-MO/AL$_2$O$_3$ CATALYST USING FIXED- AND FLUIDIZED-BED REACTORS

Prof. Dr. Abdul Halim A-K Mohammed, Chemical Engineering Department, Baghdad University
Dr. Saad Hanash Ammar, Chemical Engineering Department, Nahrain University, 2009

ABSTRACT

The present work reports a direct experimental comparison of the catalytic hydrodesulfurization of thiophene over Co-Mo/Al$_2$O$_3$ in fixed- and fluidized-bed reactors under the same conditions. An experimental pilot plant scale was constructed in the laboratories of chemical engineering department, Baghdad University; fixed-bed unit (2.54 cm diameter, and 60cm length) and fluidized-bed unit (diameter of 2.54 cm and 40 cm long with a separation zone of 30 cm long and 12.7 cm diameter). The affecting variables studied in the two systems were reaction temperature of (308 – 460) ^{o}C, Liquid hourly space velocity of (2 – 5) hr^{-1}, and catalyst particle size of (0.075-0.5) mm. It was found in both operations that the conversion increases with increasing of reaction temperature, slightly decreases with increasing of liquid hourly space velocity and not affected by particle size. Also a kinetic analysis was performed for thiophene hydrodesulfurization reaction in fixed bed reactor and the results indicate that the reaction kinetics are not affected by pore and film diffusion limitations. The results of the comparison between the two reactors indicate that a low conversion was obtained in a fluidized bed than in fixed bed over the range of conditions studied. The lower conversion can be attributed to the gas that bypasses the bed in the form of bubbles or channels.

KEYWORDS: Thiophene, Hydrodesulfurization, Fixed- bed reactor, Fluidized-bed reactor.

الخلاصة

تم في هذا البحث دراسة تفاعل هدرجة الثيوفين لازالة الكبريت بوجود عامل مساعد صلب وهو الكوبولت – موليبديوم المحمل على الالومينا.وذلك في نوعين من المفاعلات وهما المفاعل ذو الطبقة الثابتة والمفاعل ذو الطبقة المميعة. تم بناء منظومتين ريادية مكونة من مفاعل الطبقة الثابتة (ذو قطر 2,54 سم وطول 60 سم) ومفاعل الطبقة المميعة (ذو قطر 2,54 سم مطول 40 سم) الهدف من هذا الدراسة هو مقارنة اداء كل من هذين المفاعلين تحت نفس الضروف من درجة حرارة (308 -460) مْ وسرعة حجمية (2-5) سا$^{-1}$، وحجم جسيمة العامل المساعد (استخدمت ثلاث مديات لحجم جسيمة العامل المساعد:(0,075 – 0,15) ملم، (0,15 – 0,3) ملم، (0,3 – 0,5) ملم، بالاضافة للحجم الاصلي (1× (2 – 5) ملم).

اظهرت النتائج في تجارب المفاعل ذو الطبقة الثابتة تأثر التحول كثيرا بتغيير درجة حرارة التفاعل حيث يزداد التحول بزيادة درجة الحرارة ويتأثر قليلا بتغيير السرعة الحجمية ولا يتأثر بتغيير حجم جسيمة العامل الساعد. كذلك ضهرت نتائج مشابهة في تجارب المفاعل ذو الطبقة المميعة. استنتج من هذه النتائج ان حركية تفاعل هدرجة الثيوفين بوجود العامل المساعد الكوبلت - موليبيديوم المحمل على الالومينا لا تتأثر بمقاومة الانتشار الداخلي لجسيمة العامل المساعد (داخل المسامات) وكذلك لا تتأثر بمقاومة الانتشار الخارجي للجسيمة (الانتشار الغشائي).

بصورة عامة وبمقارنة الاداء بين المفاعلين، اظهرت النتائج حصول تحول اقل في المفاعل ذو الطبقة المميعة عنه في المفاعل ذو الطبقة الثابتة وذلك بسبب مرور قسم من الغاز المتفاعل الداخل خلال فقاعات او قنوات في طور الفقاعات ولا يمر على العامل المساعد في الطور المستحلب في المفاعل ذو الطبقة المميعة.

INTRODUCTION

Reactant fluid can be made to contact solid catalyst in many ways, and each has its specific advantages and disadvantages. The contacting patterns may be divided into two broad types, the fixed-bed reactors and the fluidized-bed reactors. The moving-bed reactor is an intermediate case which embodies some of the advantages and some of the disadvantages of fixed-bed and fluidized-bed reactors [1].

In comparison merits of these reactor types; in passing through fixed bed, fluid approximate plug flow. It is quite different with bubbling fluidized beds where the flow is complex and not well known, but certainly far from plug flow, and with considerable bypassing. This behavior is unsatisfactory from the standpoint of effective contacting and requires much more catalyst for high gas conversion, and greatly depresses the amount of intermediate which can be formed in series reactions. Hence, if efficient contacting in a reactor is of primary importance, then the fixed bed is favored [2].

Effective temperature control of large fixed beds can be difficult because such systems are characterized by a low heat conductivity. Thus in highly exothermic reactions hot spots or moving hot fronts are likely to develop which may ruin the catalyst. In contrast with this, the rapid mixing of solids due to bubbles and strong turbulent flow in fluidized beds allows easily and reliably controlled, practically isothermal, operations. So if operations are to be restricted within a narrow temperature range, either because of the explosive nature of the reaction or because of product distribution considerations, then the fluidized bed is favored. Fixed beds cannot use very small sizes of catalyst because of plugging and high-pressure drop, whereas fluidized beds are well able to use small-size particles. Thus for very fast reactions in which pore and film diffusion may influence the rate, the fluidized bed with its vigorous gas-solid contacting and small particles will allow a much more effective use of the catalyst [3].

If the catalyst has to be treated (regenerated) frequently because it deactivates rapidly, then the liquid-like fluidized state allows it to be pumped easily from unit to unit. This feature of fluidized contacting offers overwhelming advantages over fixed bed operations for such solids [4].

AIM OF THE PRESENT WORK

The objective of the work presented in this paper can be summarized as follows:

- Investigating the effect of fluidization on HDS reaction and comparison between the performances of fixed- and fluidized-bed reactors.
- The effect of the variables temperature, 308 – 460 °C, liquid hourly space velocity (LHSV), 2 – 5, and catalyst particle size, were studied in both types of reactors on the HDS conversion.

EXPERIMENTAL

(I)MATERIALS

- Feed

Thiophene, C_4H_4S of 99.9% purity (supplied from Fluka AG, Chem. Company) was used as a raw material for catalytic hydrodesulfurization process (molecular weight, 84; density, 1.071 gm/cm^3 at 16 °C; and boiling point, 84.1 °C).

-Catalyst

Cobalt Molybdenum supported on Alumina (**HR-306**), supplied from Middle Refineries Company, Baghdad was used as hydrodesulfurization catalyst. The physical and chemical properties of catalyst HR-306 are mentioned in Table (1). The catalyst was activated by heating in hydrogen to 350 °C and stabilized (sulfide) with thiophene and H_2 for about 2 hr.

- Gases

Hydrogen with purity of 99.9 % supplied from Middle-Electric General Company, Baghdad was used in Thiophene hydrodesulfurization process. High grade quality (purity 99.9 %) of nitrogen obtained from Al-Mansor factory, Baghdad was also used in this investigation. Nitrogen was used in the beginning in order to ensure good temperature distribution in the reactor, to purge the air from the reactor and at the end of experiment to purge off the gases from all the system.

- UNITS AND PROCEDURE

-Fixed bed system

The series of fixed bed runs were made in a conventional continuous flow fixed bed catalytic reactor unit. Schematic flow diagram of the experimental system is given in Figures 1. The equipment can be divided functionally into five parts, liquid feed dosing pump, gases feed, evaporator/ preheating, reactor system, and condensation/separation.

The fixed bed reactor consisted of a carbon steel tube (2.54 cm diameter, and 60cm length) which was charged for each experiment with about 22 gm (25.7 cm^3) sample of catalyst and placed in the middle zone while the upper and lower zones were filled with inert glass balls and work as a preheaters. The reactor was heated by four steel- Jacket heaters. Temperatures in the reactor were measured by thermocouples at three positions. The thermocouples measured the temperature profile along full length of reactor.

Before each run a 10-min nitrogen pretreatment was employed to purge the air from the system and for catalyst conditioning. The reactor is heated to the desired reaction temperature, and after reaching that temperature, the nitrogen valve was closed. After catalyst pretreatment, liquid thiophene feed was pumped by a dosing pump to the evaporator at the prespecified rate. The evaporator consists of coil tube (10m long with 5mm i.d). The heat was supplied by using 6 kW electrical heaters to vaporize and heat the feed to the desired temperature controlled by voltage regulator.

Thiophene vapor feed was mixed with hydrogen and then passed through the upper preheater and in downflow through the reactor, distributed uniformly and reacted on the catalyst. The vapor of product passed through the condenser and the condensates were collected. The reaction was allowed to proceed continuously for 30 min to permit the system to achieve a steady state conversion, pressure, and temperature. During this time the liquid product went to the waste-product receiver. After that liquid samples characterizing the run were taken over the next 20 min period. At the end of the sampling period the liquid product stream was switched to waste and the feed valves shut off.

Some gas product samples were analyzed by the gas chromatography analysis (Packard 438A located in Ibn-Sina State Company), thiophene was not detected in the gas product stream; it was present in liquid product stream only. Therefore, the percentage conversion of HDS reaction can be calculated simply from equation 1.

$$Conversion\ (\%) = \left(1 - \frac{V_A}{V_{Ao}}\right) * 100 \quad (1)$$

Where V_{Ao} is the liquid thiophene feed volume within (ml) and V_A is unreacted thiophene volume (ml) after the same period.

As preliminary experiments, the effect of duration time (time-on-stream) on catalyst activity was examined at temperature, 411 ^oC; LHSV 2 h^{-1}; catalyst particle size, 1* (2-5) mm and atmospheric pressure. The catalytic hydrodesulfurization reaction conditions employed in fixed-bed runs were reaction temperature of (308-460) ^oC, LHSV of (2 – 5) hr^{-1}, and Catalyst particle size ranges of 1* (2-5) mm, (0.5-0.3) mm, and (0.3-0.15) mm.

-Fluidized bed system

The fluidized runs were performed in an experimental fluidized bed reactor unit. Figure 2 shows the schematic flow diagram of the unit. The unit consisted of a thiophene storage tank, dosing pump, electrical evaporator, preheater to preheat the thiophene vapor and hydrogen mixture, fluidized bed reactor to contact the feed mixture and catalyst, condenser/separator to condensate and separate the unreacted thiophene, and control and power supply box.

The fluidized bed reactor was made from stainless-steel with diameter of 2.54 cm and 40 cm long with a separation zone of 30 cm long and 12.7 cm diameter. The reactor was heated electrically and the temperature was measured using thermocouples at two positions.

Perforated plate made from stainless steel with 0.5 mm thickness was used as a distributor. The distributor plate designed so as to make a free area of flow of 4.18% of the total area. The number of holes equal to 27 hole, with a hole diameter of 1 mm. A layer of a fine mesh screen was placed on the distributor to prevent the plugging of the distributor holes by the solid particles.

Before a run was started, the desired amount of catalyst was placed in the reactor and the equipment heated while nitrogen was passed upflow through the reactor. The desired amount of liquid thiophene was pumped by dosing pump to the evaporator and the vapor of thiophene was mixed with hydrogen then the mixture was preheated and entered the reactor from the bottom through the distributor. The reaction was allowed to proceed continuously for about 30 min to permit the system to achieve a steady state operation. After that liquid samples characterizing the run were taken over the next 20 min period.

The experimental conditions of fluidized-bed runs were L/D ratio of (2 – 8), reaction temperature of (308-460) ^oC, LHSV of (2 – 5) hr^{-1}, and catalyst particle size ranges of (0.075-0.15) mm, (0.15-0.3) mm, and (0.3-0.5) mm. As a preliminary study, some experiments were performed to investigate the ratio of superficial gas velocity to minimum fluidization velocity (u_o/u_{mf}) on conversion by changing L/D ratio.

Minimum fluidizing velocity experiments were carried out in a Q.V.F. glass column of 2.54 cm diameter and 40 cm long with a separation zone of 30 cm long and 12.7 cm diameter.

RESULTS AND DISCUSSION

FIXED BED RUNS

Catalyst activity

The catalytic activity (time on stream study) of Co-Mo/Al_2O_3 catalyst for the HDS of thiophene was examined in fixed bed reactor at temperature of 411 ^oC, catalyst particle size of 1*(2-5) mm, H_2 / thiophene mole ratio of 10, and LHSV of 2 hr^{-1}. Figure 3 shows the relationship between the conversions and duration time.

At first the catalyst activity increases with time during the first hour of operation properly due to the enhancement in catalyst activity by sulfiding the surface of catalyst with H_2S produced by reaction. This trend in HDS activity clearly indicates that the surface of the catalyst evolves into a more active structure during the course of the reaction. This results permit to conclude that during the reaction there is a surface sulfiding which conducts to the formation of a more active phase. Following the activity is then decreases until about 2 hr because of the accumulation of carbonaceous deposits on the catalyst surface. Then steady state activities were obtained after 2 hour of operation and remain substantially constant over a long period of time.

The same results of catalyst activity for catalytic HDS of thiophene over Co-Mo/Al_2O_3 was also observed and stated in previous studies of Kolboe and Amberg [5] and Van Parijs and Fromen [6].

Effect of liquid hourly space velocity (LHSV)

The effect of LHSV on thiophene conversion was determined at different reaction temperatures (308 to 460 ^oC), catalyst particle size of 1*(2-5) mm, and H_2 / thiophene mole ratio of 10. As shown in figure 4 the results showed that the LHSV has small effect on the conversion. At LHSV of 2 h^{-1} and temperature 308 ^oC, the conversion is 56.7% and at LHSV of 5 h^{-1} and the same temperature the conversion decreases to 45%.

As the LHSV increases thiophene conversion slightly decreases which means that the film diffusion has no effect on the reaction kinetics. These observations agree well with the results of Ghanbari et al. [7].

- Effect of Temperature

As shown in figure 5 the conversion increases as the temperature increases. At 308 ^oC and constant LHSV of 2 h^{-1}, the conversion is 56.7% while at 460 ^oC using the same LHSV the conversion reaches 78%. This is attributed to the increase of active sites that can be used for the reaction when the temperature increases. These observations agree well with the results of Kolboe and Amberg [5].

Effect of particle size

Three different particle size ranges of catalyst were used for investigation of pore diffusional limitation on the reaction kinetics of thiophene HDS. In this set of experiments the conversion of reaction was measured with different LHSV and at temperature of 360 ^oC. The results of these tests are shown in figure 6. As shown from this figure, the change in particle size range of catalyst is not affect the conversion. This indicates that the mass transfer resistance spring from pore diffusion has no effect on the reaction kinetics. This is the same observation of Ghanbari et al [7].

FLUIDIZED BED RUNS

The estimation of the minimum fluidization velocity

The pressure drop as a function of gas velocity was measured in order to obtain the values of minimum fluidization velocity for three particle sizes of catalyst, which differs from one size to another. Figures 7, 8, and 9 show the experimental determination of minimum fluidization velocity from the relation of bed pressure drop with air superficial velocity for the particle sizes of (0.075-0.15), (0.15-0.3) and (0.3-0.5) mm respectively. The values of minimum fluidization velocities become higher as the particle size increases, because of voidage increasing, which increases the quantities of the gas of necessary to fluidize these particles. Table 2 shows the experimental values of minimum fluidization velocity for the three particle sizes ranges.

Effect of superficial gas velocity

For investigation of the ratio of superficial gas velocity to minimum fluidization velocity (u_o/u_{mf}) on conversion, experiments were performed at different L/D ratio to vary the u_o/u_{mf} ratio at constant LHSV. The experimental conditions of these tests are LHSV of 2 hr^{-1}, reaction temperature of 360 ^oC, catalyst particle size range of (0.075-0.15) mm, and H_2/thiophene mole ratio of 10.

It is seen from figure 10 that conversion is slightly affected by the inlet gas velocity, even the u_o/u_{mf} ratio increases to eight times, the conversion has not varied significantly. Therefore one value of L/D ratio will be selected (L/D = 2) for the variation of LHSV experiments.

Effect of LHSV

The effect of LHSV on conversion in fluidized bed reactor was studied at different reaction temperature (308 to 460 ^oC), different particle size, L/D ratio of 2, and H_2/thiophene mole ratio of 10. Figures 11, 12, and 13 show the effect of LHSV on conversion at particle sizes of (0.075-0.15) mm, (0.15-0.3) mm, and (0.3-0.5) mm respectively. As shown in these figures, the conversion slightly decreases with increasing of LHSV. The same results were obtained in fixed bed operation and this means that the reaction rate is not affected by film diffusion step.

Effect of Temperature

Figure 14 shows the effect of temperature on conversion at different particle sizes and LHSV of 2 hr^{-1}. The conversion increases as the temperature increases. This may be attributed to the increase of active sites that can be used for the reaction when the temperature increases.

Effect of Particle size

Figure 15 shows the effect of catalyst particle size ranges on thiophene conversion. It is clear from this figure that the particle size of catalyst does not affect the thiophene conversion. The same results were obtained in fixed bed operation.

Comparison between the performances of fixed- and fluidized-bed operation

Figures 16, 17, 18, and 19 show the comparison between fixed- and fluidized-bed reactors at temperatures of 308, 360, 411, and 460 ^{o}C respectively. As shown in these figures the experimental results show that for HDS of thiophene over the range of conditions studied a lower conversion is obtained in a fluidized bed than in fixed bed. This is in agreement with the results of all workers [8-18] who also obtained lower conversion in their fluidized beds. The lower conversion can be attributed to the gas that bypasses the bed in the form of bubbles or channels and strong backmixing for both particles and gas [7, 11].

Anyway the experimental results indicate that there is indeed a range of gas velocity where there is a minimum deviation of fluidized- from fixed-bed conversion. Figures 16, 17, 18, and 19 show this phenomenon where the optimum velocity exists for the closest approach of the fluidized conversion to the fixed bed result, which is between 3 and 4 h^{-1} LHSV for the system investigated.

At relatively low gas velocities (low LHSV), channeling may take place in all or part of the bed. When a bed is channeling most of the gas is blowing through holes in a settled or bridged layer of particles. Some of the gas may be flowing through this settled layer but there is no continual agitation of the particles. Continued increase in gas velocity brings a corrective action in the turbulent intermixing between the dense and bubble phases which limits the nonuniformity of gas and catalyst composition and thus tends to bring the conversion closer to that for the fixed bed operation [10, 11].

CONCLUSIONS

The following conclusions are deduced:

- In the time on stream study, the catalyst activity increases with time of operation properly due to the enhancement in catalyst activity by sulfiding the surface of catalyst with H_2S produced by reaction. Then the activity decreases because of the accumulation of carbonaceous deposits on the catalyst surface. Finally, steady state activities were obtained after 2 hour of operation and remain substantially constant over a long period of time.
- In both reactor types, the conversion increases with increasing of reaction temperature, slightly decreases with increasing of liquid hourly space velocity (the hydrodesulfurization reaction of thiophene over Co-Mo/Al_2O_3 is not influenced by film diffusion limitation) and not affected by catalyst particle size (the reaction is not influenced by pore diffusion limitation).
- The results indicate that a low conversion was obtained in a fluidized bed than in fixed bed over the range of conditions studied. The lower conversion can be attributed to the gas that bypasses the bed in the form of bubbles or channels and strong backmixing for both particles and gas.

REFERENCES

- Davidson, J.F. and Harrison, D. "Fluidization", Academic Press, London, (1971).
- Kunii D. and Levenspiel O., "Fluidization Engineering", Krieger Publishing Co., New York, (1977).
- Smith J. M., "Chemical Engineering Kinetics", 3^{ed} ed., McGraw-HILL, London, (1981).
- Charles G. H., "An introduction to chemical engineering kinetics and reactor design", JOHN WILEY & SONS, New York, (1977).
- Kolboe S. and Amberg C. H., Canadian Journal of Chemistry. Volume 44 (1966).
- Van Parijs I. A. and Fromen G. F., Ind. Eng. Chem. Prod. Res. Dev., Vol. 25, No. 3, (1986).
- Ghanbari K. and et. al. Petroleum & Coal 48(2) 33-36 (2006)

Johnstone, H. F., Batchlor, J. D., Shen, C. Y., A.I.Ch.E. J., 1, 318 (1955).

- Shen, C. Y., Johnstone, H. F., A.I.Ch.E. Journal, 1, 349 (1955).
- Mathis J. F., Watson C. C., A.I.Ch.E. Journal, Vol. 2, No. 2, 518 (1956).
- Ishii,T., Osberg,G. L., A.I.Ch.E. J., 11, 279 (1965).
- Lewis W. K., Gilliland E. R., and Werner G., A.I.Ch.E. Journal, Vol. 5, No. 4 (1959)
- Gomezplata A. and Shuster W., A.I.Ch.E. Journal, 6, 454 (1960).
- Weekman V. W. and Donald M. N., A.I.Ch.E. Journal, Vol. 16 No. 3 (1970).
- Nace, D. M., Voltz, S. E., Weekman, V. W., Jr., Ind. Eng. Chem. Process Des. Develop, 10, 530 (1971).
- Benjamin G., Donald M., and Sterling E., Ind. Eng. Progress, Des. Develop, Vol. 13, No. 3, (1974).
- James H. Edwards, Ralph J. Tyler, and Stephen D. White, Energy & Fuels, Val. 4, No. 1, (1990).
- Wagialla K. M. and S Elnashaie S. E. H., Ind. Eng. Chem. Res., Vol. 30, No. 10, (1991).

Table 1: Properties of catalyst HR-306

Surface area (m^2/gm)	280
Pore volume (cc/gm)	0.55
Cobalt (wt %)	4
Molybdenum (wt %)	12
Density (g/cm^3)	0.6
Manufacturer	Procatalyse

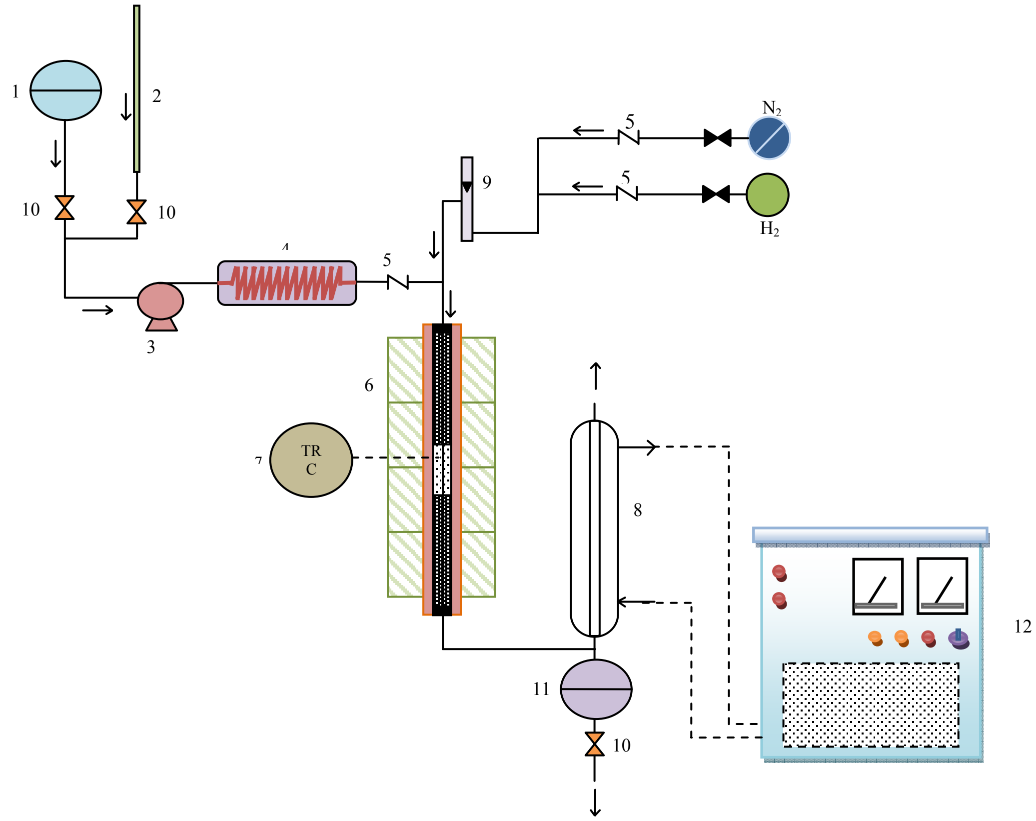


Fig. 1 Schematic flow diagram of the fixed bed reactor unit: (1) Feed reservoir; (2) Metering buret; (3) Dosing pump; (4) Evaporator; (5) One way valve; (6) Reactor system; (7) Temperature

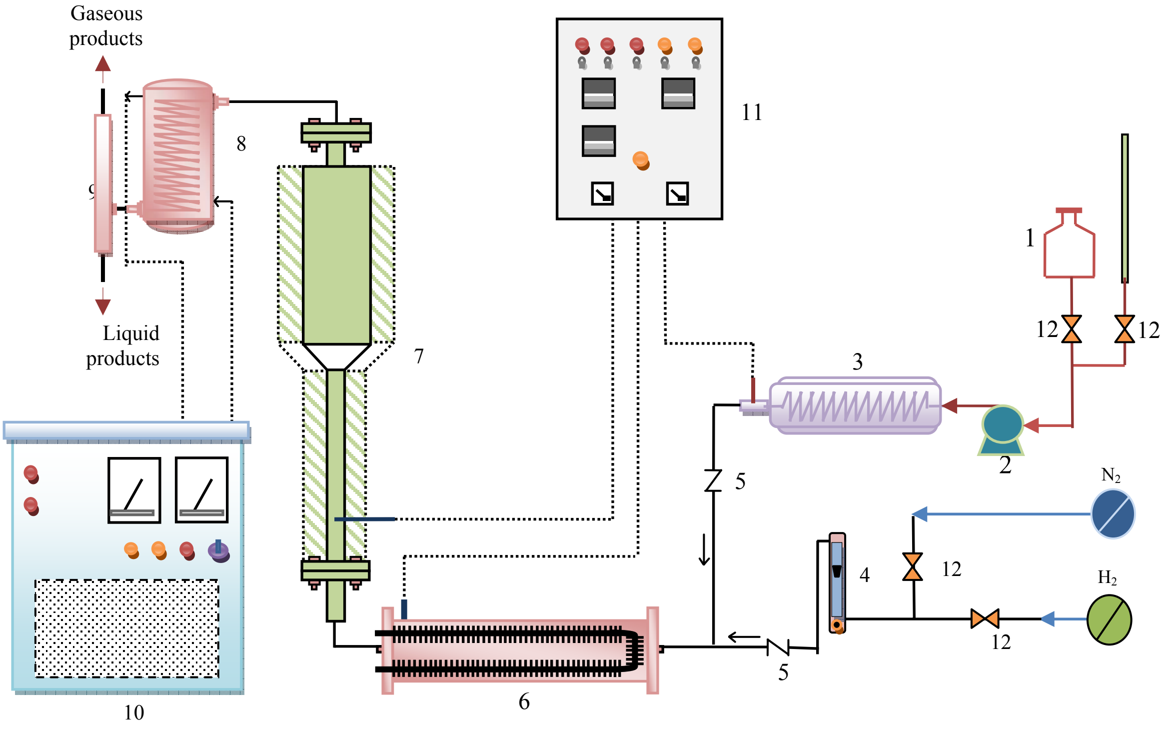


Fig. 2 Schematic flow diagram of the fluidized bed reactor unit: (1) Feeding tank; (2) Dosing pump; (3) Evaporator; (4) Gas flow meter; (5) One way valve; (6) Preheater; (7) Fluidized bed reactor; (8) Condenser; (9) Gas-liquid separator; (10) Chiller; (11) Control and power supply box; (12) Valve.

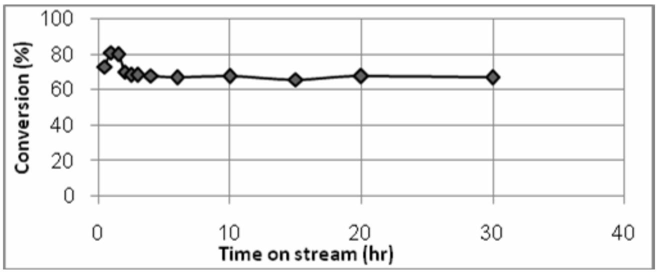


Fig. 3 Hydrodesulfurization of Thiophene over Co-Mo/Al_2O_3 at 411^{o}C (fixed bed operation).

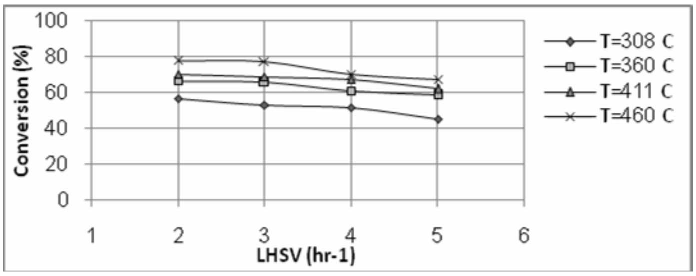


Fig. 4 Effect of LHSV on thiophene conversion at different temperatures (fixed bed operation)

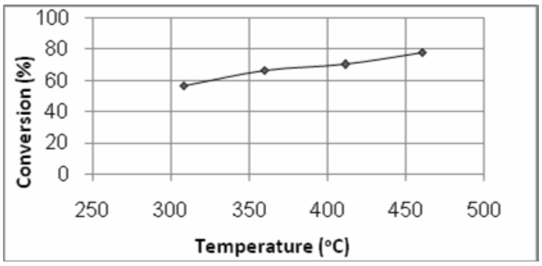


Fig. 5 Effect of Temperature on Thiophene Conversion at LHSV 2 hr^{-1} (fixed bed operation).

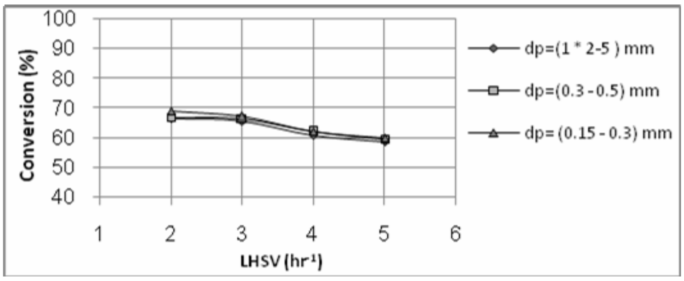
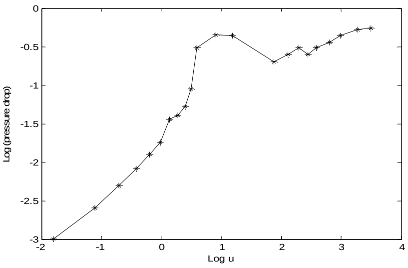


Fig. 6 Effect of Catalyst particle size on Thiophene Conversion at different LHSV and at temperature of 360 ^{o}C (fixed bed operation).



Fig, 7 Relationship between bed pressure drop and superficial velocity for particle size of (0.075-0.15) mm.

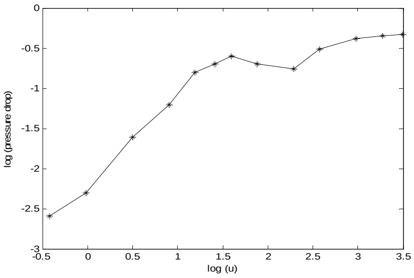


Fig. 8 Relationship between bed pressure drop and superficial velocity for particle size of (0.15-0.3) mm.

•

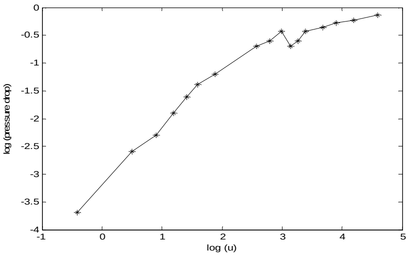


Fig. 9 Relationship between bed pressure drop and superficial velocity for particle size of (0.3-0.5) mm.

Table 2 Experimental values of minimum fluidization velocity

Particle size (mm)	u_{mf} (cm/s)
0.075-0.15	6.04
0.15-0.3	9.974
0.3-0.5	24.5

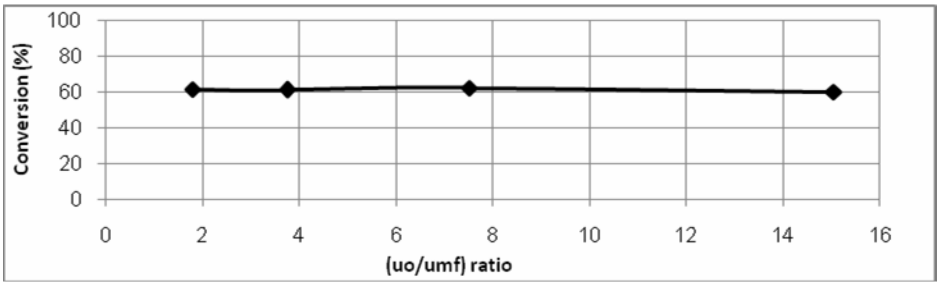


Fig. 10 Effect of u_o/u_{mf} ratio on conversion (fluidized bed operation).

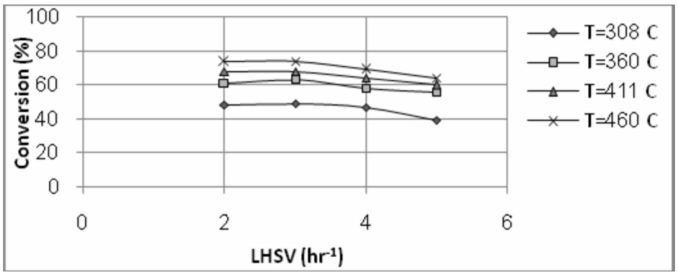


Fig. 11: Effect of LHSV on conversion at different temperatures and at particle size of (0.075-0.15) mm (fluidized bed operation).

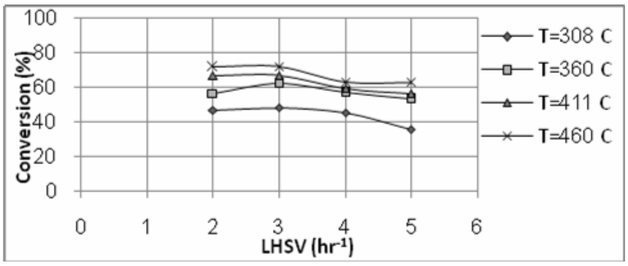


Fig. 12: Effect of LHSV on conversion at different temperatures and at particle size of (0.15-0.3) mm (fluidized bed operation).

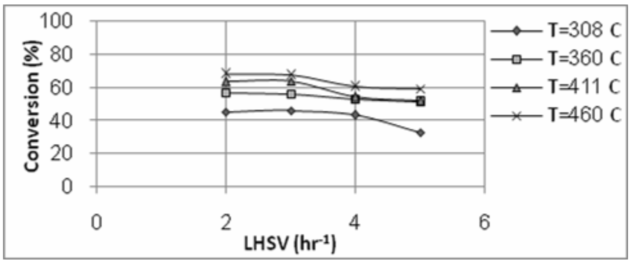


Fig. 13: Effect of LHSV on conversion at different temperatures and at particle size of (0.3-0.5) mm (fluidized bed operation).

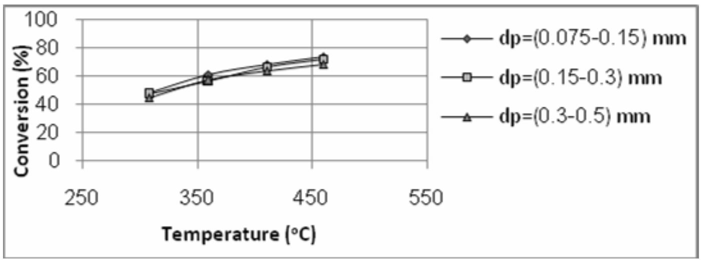


Fig. 14: Effect of temperature on conversion at different particle size and at LHSV of 2 hr^{-1} (fluidized bed operation).

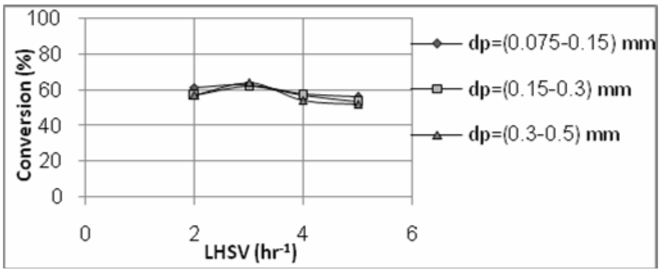


Fig. 15: Effect of particle size on conversion at different LHSV and at temperature of 360 °C (fluidized bed operation).

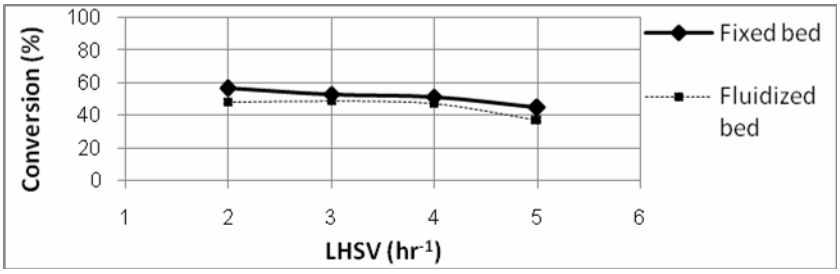


Fig. 16 Conversion as a function of LHSV for fluidized operation compared with fixed bed operation at temperature of 308 °C.

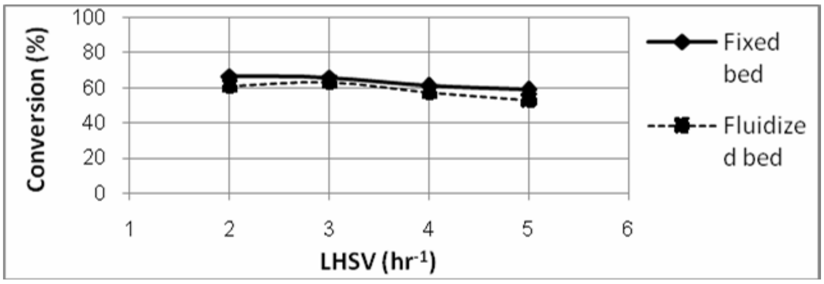


Fig.17 Conversion as a function of LHSV for fluidized operation compared with fixed bed operation at temperature of 360 °C.

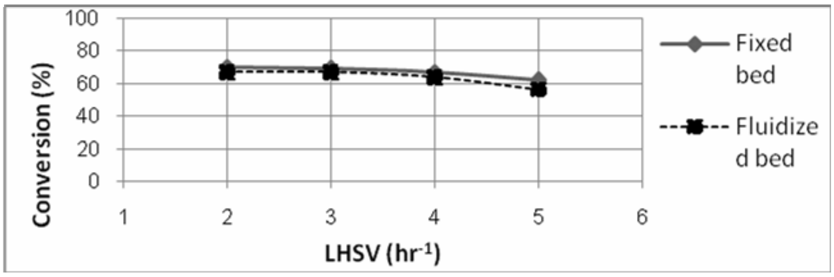


Fig. 18 Conversion as a function of LHSV for fluidized operation compared with fixed bed operation at temperature of 411 °C.

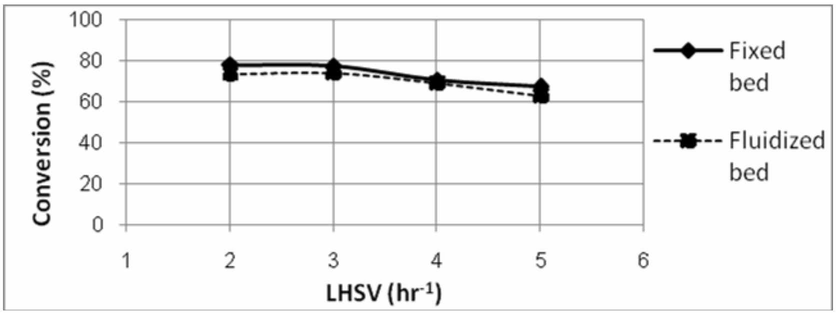


Fig.19 Conversion as a function of LHSV for fluidized operation compared with fixed bed operation at temperature of 460 °C.