

## CHAPTER 4



### RESULTS AND DISCUSSION

#### 4.1 COMPARISON OF HYDRODESULFURIZATION ACTIVITY BETWEEN SELF-PREPARED AND INDUSTRIAL CATALYSTS

In this study experiments were carried out to compare the activity of the cobalt-molybdate type catalysts between two self-prepared and one industrial catalysts. From the literature we learned that molybdenum was a necessary constituent of a hydrodesulfurization catalyst, that a combination of cobalt and molybdenum was more active than molybdenum alone. Cobalt was generally described as promoter, and the amount of cobalt had remarkable effect on hydrodesulfurization activity.

In order to investigate this promoter effect we prepared two catalyst samples (SELF-1 and SELF-2) that contained the same amount of molybdenum but different amounts of cobalt and compared their hydrodesulfurization activity among themselves and the industrial catalyst sample from Thai Oil Co.,Ltd. (TOC-CAT). The compositions of the catalysts were shown in Table 4.1.

Table 4.1 Composition of the tested catalysts

Composition	TOC-CAT	SELF-1	SELF-2
Co(wt.%)	2.4	10.28	5.30
Mo(wt.%)	9.9	12.35	12.71
Co/(Co+Mo)	0.2	0.45	0.29

In order to compare the activity of these catalysts, the following severe conditions were chosen to ensure deep hydrodesulfurization. So that we chose the strongest condition that was study about thiophene hydrodesulfurization as reported by Ignace A. Van Parijs and Gilbert F. Froment(1986). The experimental conditions were :

Toluene containing thiophene about 500-600 ppm as feed

Total pressure = 30 bars

Molar ratio of hydrogen to feed = 10:1

Liquid hourly space velocity = 2.6 hr<sup>-1</sup>

The temperature of each experiment was varied to find the minimum temperature at which deep hydrodesulfurization was observed.

#### 4.1.1 Catalyst Sample from Thai Oil Co.,Ltd.(TOC-CAT)

The hydrodesulfurization activity of TOC-CAT was studied at temperatures between 230–300 °C. The results were shown in Table 4.2.

The successive temperatures for TOC-CAT were 300, 250, 270, 230, and repeated at 250 °C to check if the effect of temperature increase and decrease on hydrodesulfurization activity was insignificant. The experimental results showed that at 300 °C, about 520 ppm thiophene in the feed was completely removed. At 250, 270, and 230 °C, thiophene conversion was only 90 %, 96 % and 74 % by wt., respectively, as shown in Fig. 4.1.

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TABLE 4.2 THIOPHENE CONVERSION AS FUNCTION OF  
 REACTION TIME AT VARIOUS TEMPERATURES FOR  
 TOC-CAT AT P=30 BARS LHSV = 2.6 HR<sup>-1</sup>

TIMES (HOURS)	TEMP.= 300 °C		TEMP.= 250 °C		TEMP.= 270 °C		TEMP.= 230 °C		TEMP.= 250 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	519.97	0.00	519.97	0.00	519.97	0.00	519.97	0.00	519.97	0.00
0.50	0.00	100.00	341.06	34.41	243.13	53.24	108.81	79.07	73.75	85.82
2.00	0.00	100.00	48.63	90.65	21.61	95.84	125.55	75.85	56.83	89.07
4.00	0.00	100.00	35.54	93.17	18.55	96.43	117.64	77.38	55.30	89.37
6.00	0.00	100.00	34.15	93.43	18.06	96.53	139.17	73.24	53.06	89.79
8.00	0.00	100.00	42.41	91.84	17.72	96.59	131.53	74.70	50.43	90.30
10.00	0.00	100.00	51.77	90.04	17.59	96.62	130.97	74.81	49.57	90.47



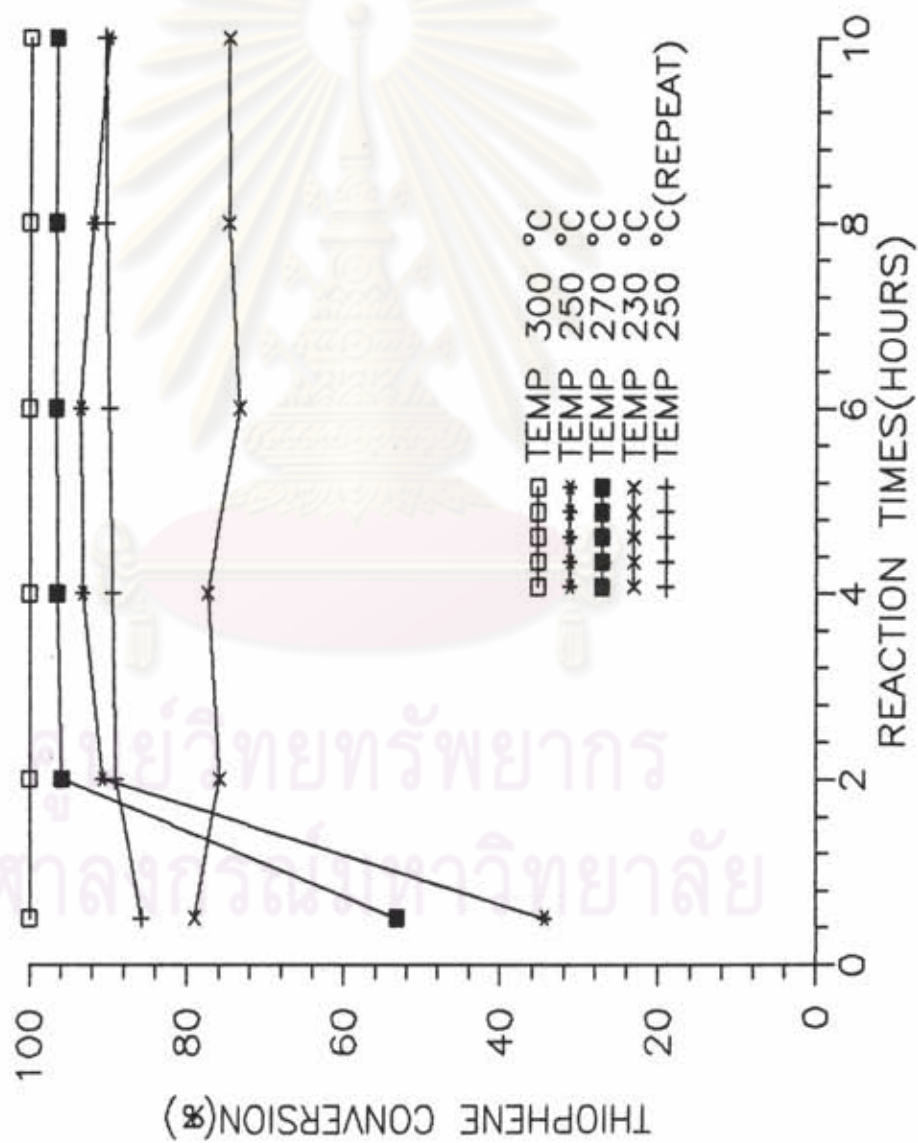


FIGURE. 4.1 THIOPHENE CONVERSION VS REACTION TIMES OF TOC-CAT (P=30 BARS LHSV=2.6 HR<sup>-1</sup>)

#### 4.1.2 Self-prepared catalyst no.1 (SELF-1)

The hydrodesulfurization activity of SELF-1 was studied at temperatures between 250-290 °C. The results were shown in Table 4.3.

The successive temperatures for SELF-1 were 270, 290, 250, 260, and repeated at 270 °C to see if the effect of temperature increase and decrease on hydrodesulfurization activity was insignificant. The experimental results showed that at 290 °C, about 590 ppm thiophene in the feed was completely removed. At 270, 250, and 260 °C, thiophene conversion was only 96 %, 88 % and 90 % by wt., respectively, as shown in Fig 4.2.



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TABLE 4.3 THIOPHENE CONVERSION AS FUNCTION OF  
 REACTION TIME AT VARIOUS TEMPERATURES FOR  
 SELF-1 CATALYST AT P=30 BARS LHSV = 2.6 HR<sup>-1</sup>

TIMES (HOURS)	TEMP. = 270°C		TEMP. = 290°C		TEMP. = 250°C		TEMP. = 260°C		TEMP. = 270°C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	588.73	0.00	588.73	0.00	588.73	0.00	588.73	0.00	588.73	0.00
0.50	311.72	47.05	1027.00	98.26	265.52	54.90	116.98	80.13	40.40	93.14
2.00	53.08	90.98	6.38	98.92	64.82	88.99	51.21	91.30	34.57	94.13
4.00	28.85	95.10	0.00	100.00	65.85	88.82	54.18	90.80	41.16	93.01
6.00	21.47	96.35	0.00	100.00	73.37	87.54	56.82	90.35	40.61	93.10
8.00	20.23	96.56	0.00	100.00	68.45	88.37	62.80	89.33	45.03	92.35
10.00	20.62	96.50	0.00	100.00	60.63	89.70	65.62	88.85	40.54	93.11

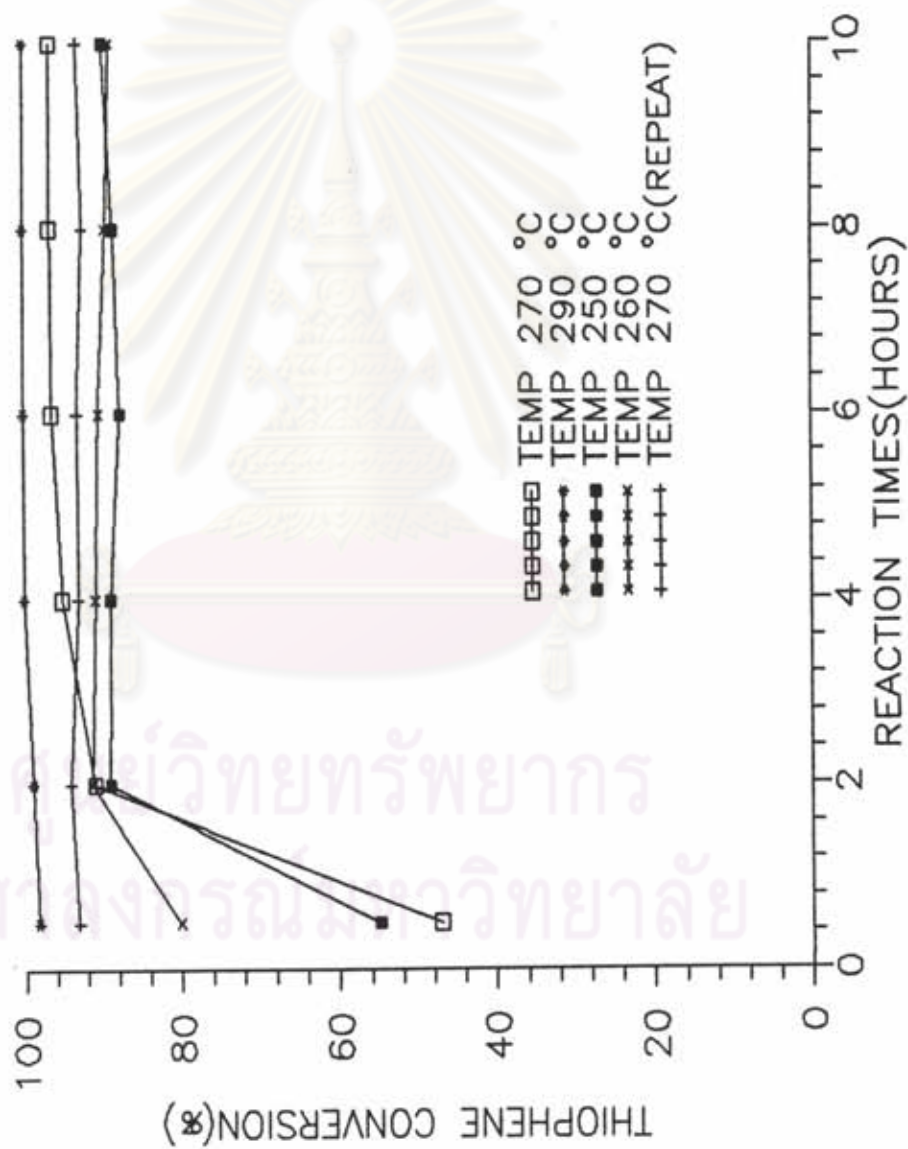


FIGURE. 4.2 THIOPHENE CONVERSION VS REACTION TIMES OF SELF-1 CATALYST (P=30 BARS LHSV=2.6 HR<sup>-1</sup>)





#### 4.1.3 Self-prepared catalyst no.2 (SELF-2)

The hydrodesulfurization activity of SELF-1 was studied at temperatures between 250–280 °C. The results were shown in Table 4.4.

The successive temperatures for SELF-1 were 280, 270, 260, 250, and repeated at 270 °C to see if the effect of temperature increase and decrease on hydrodesulfurization activity was insignificant. The experimental results showed that at 280, 270, and 260 °C, about 525 ppm thiophene in the feed was completely removed after 2, 4, and 8 hrs, respectively. At 250 °C, thiophene conversion was only 95 %, as shown in Fig 4.3.



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TABLE 4.4 THIOPHENE CONVERSION AS FUNCTION OF REACTION TIME AT VARIOUS TEMPERATURES FOR SELF-2 CATALYST AT P=30 BARS LHSV = 2.6 HR<sup>-1</sup>

TIMES (HOURS)	TEMP.= 280 °C		TEMP.= 270 °C		TEMP.= 260 °C		TEMP.= 250 °C		TEMP.= 270 °C(REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00
0.50	147.89	71.82	28.97	94.48	183.17	65.10	165.92	68.39	7.30	98.61
2.00	0.00	100.00	4.33	99.18	11.89	97.73	22.96	95.62	4.33	99.18
4.00	0.00	100.00	0.00	100.00	7.60	98.55	27.88	94.69	0.00	100.00
6.00	0.00	100.00	0.00	100.00	7.53	98.57	25.42	95.16	0.00	100.00
8.00	0.00	100.00	0.00	100.00	0.00	100.00	27.18	94.82	0.00	100.00
10.00	0.00	100.00	0.00	100.00	0.00	100.00	24.99	95.24	0.00	100.00

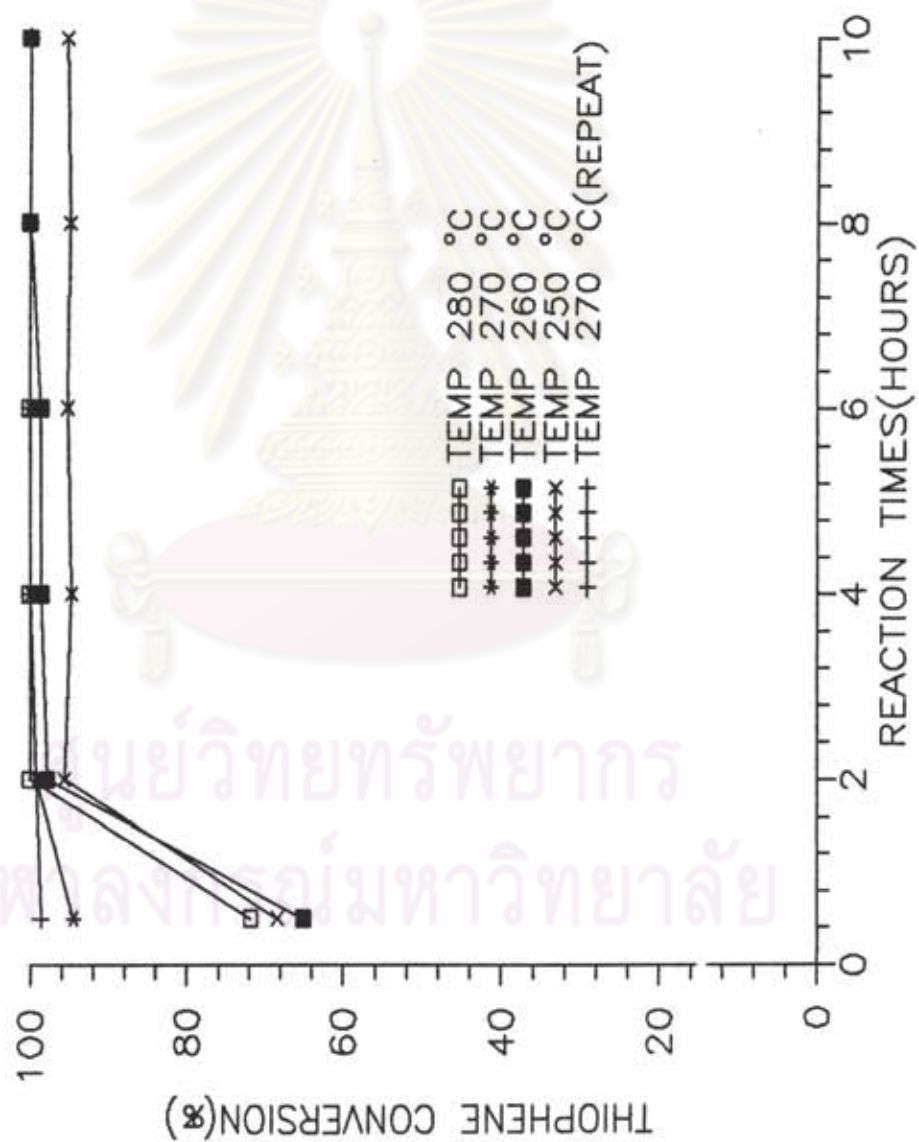


FIGURE 4.3 THIOPHENE CONVERSION VS REACTION TIMES OF SELF-2 CATALYST (P=30 BARS LHSV=2.6 HR<sup>-1</sup>)

#### 4.1.4 Conclusion on Comparative Activity

From the above experimental results, it was found that deep hydrodesulfurization of thiophene in toluene for SELF-1 and SELF-2 catalysts occurred at 290, and 270 °C, respectively. It founded that SELF-2 was equally active at lower temperature than SELF-1. So that it shown that further increased of cobalt content from 5.3 to 10.28 led to decreased activity of hydrodesulfurization. When compare with TOC-CAT, it was found that deep hydrodesulfurization of thiophene in toluene occurred at 300°C. Obviously SELF-2 was equally active at the lowest temperature, so that SELF-2 was the most active among the three. The conclusion was in agreement with the report by Hagenbach et. al (1973) which stated that cobalt molybdate catalyst was most active when the ratio  $Co/(Co+Mo)$  equalled 0.3-0.4. As seen from Table 4.1  $Co/(Co+Mo)$  of SELF-2 was about 0.29, whereas for SELF-1 and TOC-CAT it was 0.45, and 0.2, respectively.

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#### 4.2 EFFECT OF REACTION CONDITIONS ON HYDRODESULFURIZATION OF THE SYNTHETIC FEED

In order to investigate the individual effect of temperature, pressure and space velocity on hydrodesulfurization using the SELF-2 catalyst, the following experimental conditions were used:

Toluene containing thiophene about 500–600 ppm as feed

Total pressure = 10,20,30 bars

Molar ratio of hydrogen to feed = 10:1

Liquid hourly space velocity = 2.6,4,6 hr<sup>-1</sup>

The temperature of each experiment was varied to find the minimum temperature at which deep hydrodesulfurization was observed.

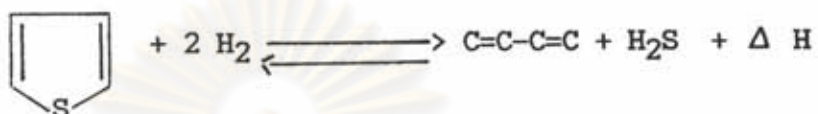
##### 4.2.1 The effect of pressure

As shown in Tables 4.5 - 4.7, the obtained results based on the same space velocity show that the higher the pressure, the lower the temperature required to completely remove thiophene from the feed. For example, for LHSV = 4 and total pressure = 30, 20, and 10 bars, the results showed that about 525 ppm thiophene in the feed was completely removed at 250, 260, and 280 °C, respectively, as shown in Figs. 4.4 - 4.6 or Table 4.6.

When compared at the same temperature and space velocity, i.e., at 270 °C and LHSV = 2.6, for the total pressure = 30, 20, 10



bars the removal efficiency of thiophene from the feed reached 100% after 4 hrs, 100% after 8 hrs, and only 96% after 10 hrs, respectively (see Table 4.5). These results could partly be explained by the reaction equation as below:



when increased pressure the system will occur in the path way that decrease the pressure that is path way to the thiophene remove. So that when increase pressure , the thiophene conversion increase.

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TABLE 4.5 THIOPHENE CONVERSION AS FUNCTION OF REACTION TIME AT VARIOUS PRESSURES FOR SELF-2 AT LHSV = 2.6 HR<sup>-1</sup>  
P = 30 BARS

TIMES (HOURS)	TEMP. = 280 °C		TEMP. = 270 °C		TEMP. = 260 °C		TEMP. = 250 °C		TEMP. = 270 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00
0.50	147.89	71.82	28.97	94.48	183.17	65.10	165.92	68.39	7.30	98.61
2.00	0.00	100.00	4.33	99.18	11.89	97.73	22.96	95.62	4.33	99.18
4.00	0.00	100.00	0.00	100.00	7.60	98.55	27.88	94.69	0.00	100.00
6.00	0.00	100.00	0.00	100.00	7.53	98.57	25.42	95.16	0.00	100.00
8.00	0.00	100.00	0.00	100.00	0.00	100.00	27.18	94.82	0.00	100.00
10.00	0.00	100.00	0.00	100.00	0.00	100.00	24.99	95.24	0.00	100.00

P = 20 BARS

TIMES (HOURS)	TEMP. = 270 °C		TEMP. = 280 °C		TEMP. = 290 °C		TEMP. = 260 °C		TEMP. = 290 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00
0.50	143.89	72.68	18.31	96.51	0.00	100.00	138.15	73.68	12.94	95.73
2.00	11.22	97.86	11.22	97.86	0.00	100.00	44.74	91.48	13.09	97.51
4.00	8.25	98.43	11.84	97.74	0.00	100.00	35.72	93.19	12.05	97.71
6.00	7.74	98.52	0.00	100.00	0.00	100.00	33.85	93.55	14.51	97.24
8.00	0.00	100.00	0.00	100.00	0.00	100.00	34.58	93.41	13.59	97.41
10.00	0.00	100.00	0.00	100.00	0.00	100.00	37.71	92.82	22.70	95.67

P = 10 BARS

TIMES (HOURS)	TEMP. = 270 °C		TEMP. = 280 °C		TEMP. = 290 °C		TEMP. = 300 °C		TEMP. = 290 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00	524.85	0.00
0.50	246.30	53.07	12.72	97.58	178.50	65.99	171.02	67.41	158.47	69.81
2.00	25.44	95.15	11.26	97.86	13.19	97.49	0.00	100.00	13.31	97.46
4.00	17.78	96.61	9.92	98.11	0.00	100.00	0.00	100.00	9.55	98.18
6.00	20.22	96.15	10.37	98.02	0.00	100.00	0.00	100.00	10.60	97.98
8.00	19.95	96.20	5.96	98.86	0.00	100.00	0.00	100.00	9.62	98.17
10.00	21.25	95.95	10.64	97.97	0.00	100.00	0.00	100.00	7.86	98.50



TABLE 4.6 THIOPHENE CONVERSION AS FUNCTION OF REACTION TIME AT VARIOUS PRESSURES FOR SELF-2 AT LHSV = 4 HR<sup>-1</sup>  
P = 30 BARS

TIMES (HOURS)	TEMP. = 260 °C		TEMP. = 250 °C		TEMP. = 240 °C		TEMP. = 250 °C (REPEAT)		TEMP. = 230 °C	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	507.35	0.00	507.35	0.00	507.35	0.00	507.35	0.00	507.35	0.00
0.50	117.37	76.87	0.00	100.00	149.15	70.60	93.45	81.58	96.90	80.90
2.00	0.00	100.00	0.00	100.00	13.48	97.34	0.00	100.00	53.02	89.55
4.00	0.00	100.00	0.00	100.00	29.50	94.19	0.00	100.00	36.54	92.80
6.00	0.00	100.00	0.00	100.00	25.07	95.06	0.00	100.00	51.15	89.92
8.00	0.00	100.00	0.00	100.00	61.01	87.97	0.00	100.00	67.71	86.65
10.00	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00	32.33	93.63

P = 20 BARS

TIMES (HOURS)	TEMP. = 270 °C		TEMP. = 250 °C		TEMP. = 260 °C		TEMP. = 240 °C		TEMP. = 260 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	507.35	0.00	507.35	0.00	507.35	0.00	507.35	0.00	507.35	0.00
0.50	18.02	96.45	164.33	67.61	0.00	100.00	104.58	79.39	0.00	100.00
2.00	0.00	100.00	23.85	95.30	0.00	100.00	40.01	92.11	0.00	100.00
4.00	0.00	100.00	12.02	97.63	0.00	100.00	23.67	95.33	0.00	100.00
6.00	0.00	100.00	13.26	97.39	0.00	100.00	33.41	93.42	0.00	100.00
8.00	0.00	100.00	16.71	96.71	0.00	100.00	35.70	92.96	0.00	100.00
10.00	0.00	100.00	13.83	97.27	0.00	100.00	20.46	95.97	0.00	100.00

P = 10 BARS

TIMES (HOURS)	TEMP. = 250 °C		TEMP. = 280 °C		TEMP. = 270 °C		TEMP. = 290 °C		TEMP. = 300 °C	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00
0.50	209.98	56.19	18.29	96.18	260.05	45.74	80.35	83.23	177.91	62.88
2.00	53.64	88.81	8.30	98.27	24.30	94.93	8.14	98.30	4.72	99.02
4.00	97.60	79.63	0.00	100.00	33.22	93.07	0.00	100.00	0.00	100.00
6.00	92.02	80.80	0.00	100.00	20.12	95.80	0.00	100.00	0.00	100.00
8.00	137.22	71.37	0.00	100.00	17.95	96.25	0.00	100.00	0.00	100.00
10.00	77.90	83.75	0.00	100.00	13.35	97.21	0.00	100.00	0.00	100.00

TABLE 4.7 THIOPHENE CONVERSION AS FUNCTION OF  
 REACTION TIME AT VARIOUS PRESSURES FOR SELF-2 AT LHSV = 6 HR  
 P = 30 BARS

TIMES (HOURS)	TEMP.= 250°C		TEMP.= 270°C		TEMP.= 280°C		TEMP.= 240°C		TEMP.= 260°C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00
0.50	147.70	69.18	0.00	100.00	120.16	74.93	69.57	85.48	339.92	29.07
2.00	38.97	91.87	0.00	100.00	0.00	100.00	60.33	87.41	18.84	96.07
4.00	36.49	92.39	0.00	100.00	0.00	100.00	116.57	75.68	10.03	97.91
6.00	18.49	96.14	0.00	100.00	0.00	100.00	60.79	87.32	10.26	97.86
8.00	22.86	95.23	0.00	100.00	0.00	100.00	86.03	82.05	10.97	97.71
10.00	21.85	95.44	0.00	100.00	0.00	100.00	57.25	88.05	10.95	97.72

P = 20 BARS

TIMES (HOURS)	TEMP.= 290°C		TEMP.= 270°C		TEMP.= 280°C		TEMP.= 280°C (REPEAT)		TEMP.= 260°C	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00	479.25	0.00
0.50	42.54	91.12	102.19	78.68	0.00	100.00	100.71	78.99	33.18	93.08
2.00	0.00	100.00	10.61	97.79	0.00	100.00	0.00	100.00	21.02	95.61
4.00	0.00	100.00	9.94	97.63	0.00	100.00	0.00	100.00	20.15	95.80
6.00	0.00	100.00	8.88	98.15	0.00	100.00	0.00	100.00	25.49	94.68
8.00	0.00	100.00	7.82	98.37	0.00	100.00	0.00	100.00	31.01	93.53
10.00	0.00	100.00	7.53	98.43	0.00	100.00	0.00	100.00	24.07	94.98

P = 10 BARS

TIMES (HOURS)	TEMP.= 280°C		TEMP.= 300°C		TEMP.= 310°C		TEMP.= 330°C		TEMP.= 320°C	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	478.24	0.00	478.24	0.00	478.24	0.00	478.24	0.00	478.24	0.00
0.50	209.20	56.26	26.22	94.52	96.38	79.85	0.00	100.00	134.01	71.98
2.00	84.35	82.36	13.64	97.15	14.27	97.02	7.65	98.40	16.42	96.57
4.00	54.88	88.52	8.54	98.21	13.53	97.17	0.00	100.00	14.36	97.00
6.00	72.36	84.87	14.26	97.02	17.33	96.38	0.00	100.00	17.46	96.35
8.00	47.83	90.00	12.39	97.41	10.38	97.83	0.00	100.00	16.40	96.57
10.00	48.61	89.84	10.98	97.70	10.36	97.83	0.00	100.00	16.28	96.60



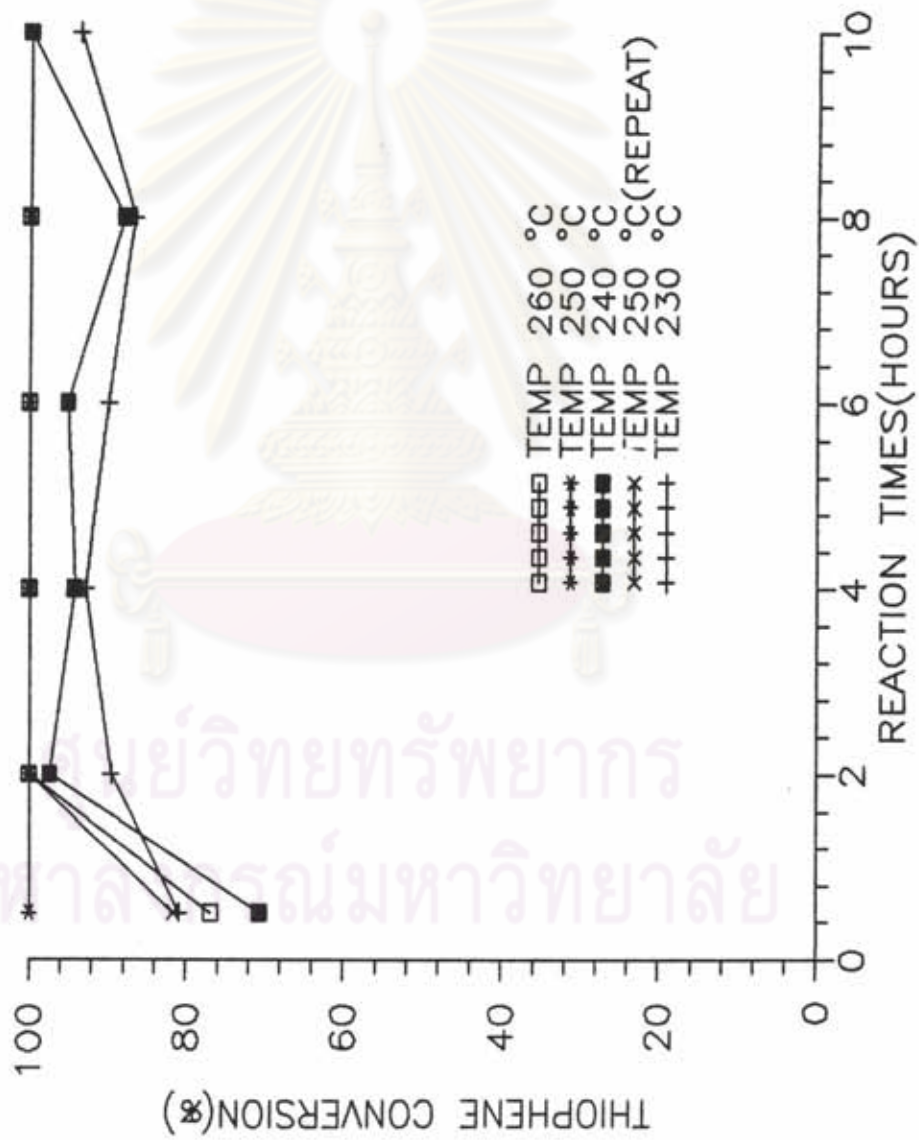


FIGURE 4.4 THIOPHENE CONVERSION VS REACTION TIMES OF SELF-2 CATALYST (P=30 BARS LHSV=4 HR<sup>-1</sup>)



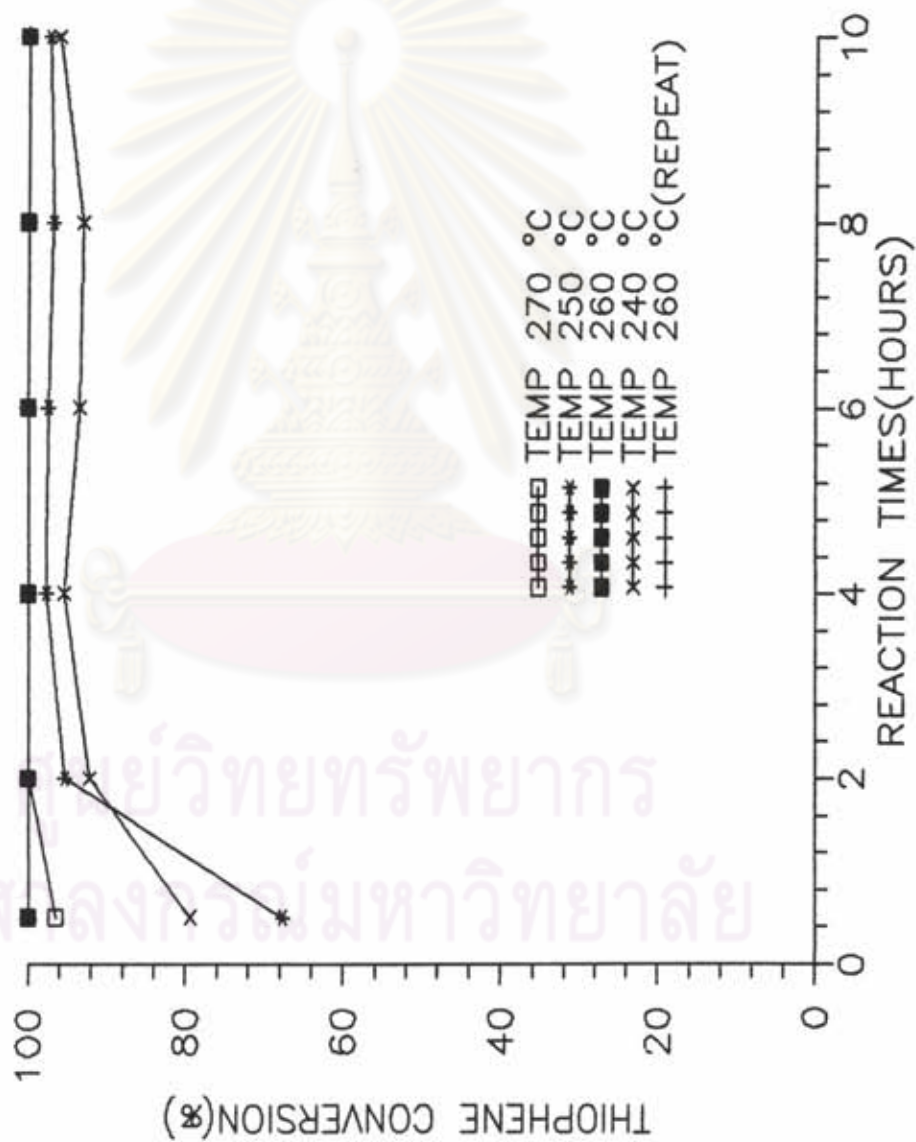


FIGURE 4.5 THIOPHENE CONVERSION VS REACTION TIMES OF SELF-2 CATALYST (P=20 BARS LHSV=4 HR<sup>-1</sup>)

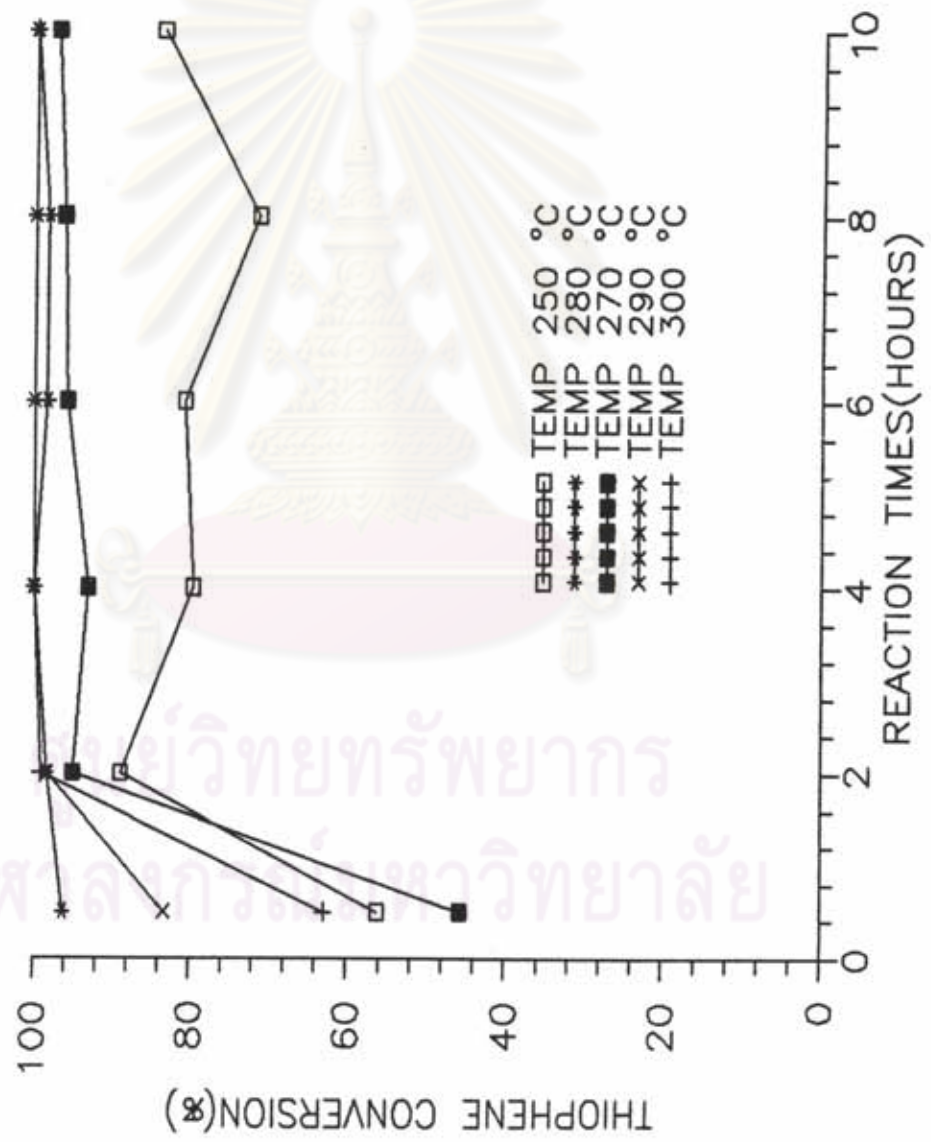


FIGURE 4.6 THIOPHENE CONVERSION VS REACTION TIMES OF SELF-2 CATALYST (P=10 BARS LHSV=4 HR<sup>-1</sup>)

#### 4.2.2 Effect of space velocity

The effect of space velocity (2.6 to 6 hr<sup>-1</sup>) has been investigated at 10, 20, and 30 bars. The results are summarized in Table 4.8. It was found that the medium space velocity LHSV= 4 had the highest thiophene conversion, as shown in Fig. 4-7. We found that when LHSV decreased from 6 to 4 hr<sup>-1</sup>, the contact time increased so that the conversion increased.



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TABLE 4.8 THIOPHENE CONVERSION AS FUNCTION OF SPACE VELOCITY

SPACE VELOCITY (HR )	AT P= 10 BARS. 300 °C			AT P= 20 BARS. 260 °C			AT P= 30 BARS. 250 °C		
	CONVERSION * (%)			CONVERSION * (%)			CONVERSION * (%)		
2.6	100			92.82			95.24		
4	100			100			100		
6	97.7			94.98			95.44		

\* STEADY CONVERSION VALUE AFTER 10 HOURS ON-STREAM

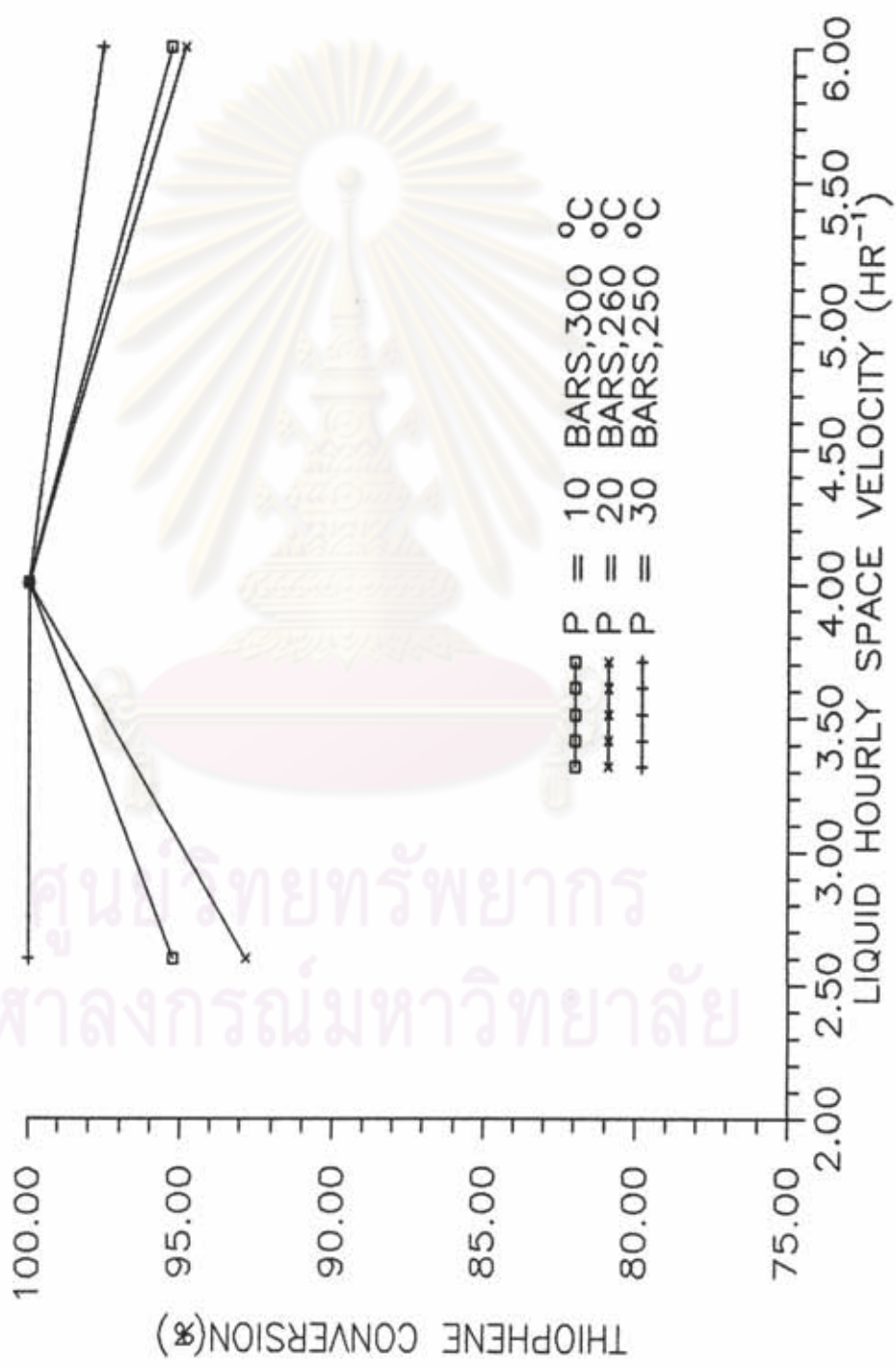


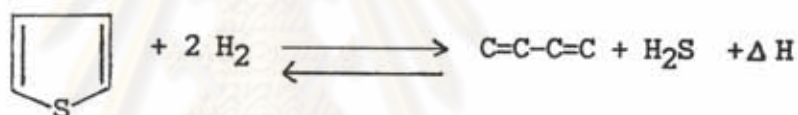
FIGURE 4.7 THIOPHENE CONVERSION VS LIQUID HOURLY SPACE VELOCITY

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### 4.2.3 Effect of temperature

From the experimental results shown in Tables 4.9 - 4.11, and in Figs. 4.8 - 4.10, it was found that the higher the temperature, the higher the thiophene removal efficiency. For example, at 20 bars (see Table 4.5) the time required to achieve steady complete conversion of thiophene was found to be 8, 4, 0.5 hours at 270, 280, 290 °C, respectively. The conclusion could partly be explained by the reaction equation below:



When temperature increases an exothermic system will shift in the direction that decreases the temperature, in this case the backward reaction of hydrodesulfurization. So conversion of thiophene will decrease. On the other hand, a higher temperature the rate of forward and backward reaction increased so the system came to an equilibrium at a much shorter time than at a lower temperature.

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TABLE 4.9 THIOPHENE CONVERSION AFTER 10 HOURS AS FUNCTION OF TEMPERATURE AT  $LHSV = 2.6 \text{ HR}^{-1}$

TEMP. (°C)	P = 10 BARS	P = 20 BARS	P = 30 BARS
	CONVERSION (%)	CONVERSION (%)	CONVERSION (%)
250			95.24
260		92.82	100.00
270	95.95	100.00	100.00
280	97.97	100.00	100.00
290	100.00	100.00	
300	100.00	100.00	

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TABLE 4.10 THIOPHENE CONVERSION AFTER 10 HOURS AS FUNCTION OF TEMPERATURE AT LHSV = 4 HR<sup>-1</sup>

TEMP. (°C)	P = 10 BARS	P = 20 BARS	P = 30 BARS
	CONVERSION (%)	CONVERSION (%)	CONVERSION (%)
230			93.63
240		95.97	100.00
250		97.27	100.00
260		100.00	100.00
270	97.21	100.00	
280	100.00		
290	100.00		
300	100.00		

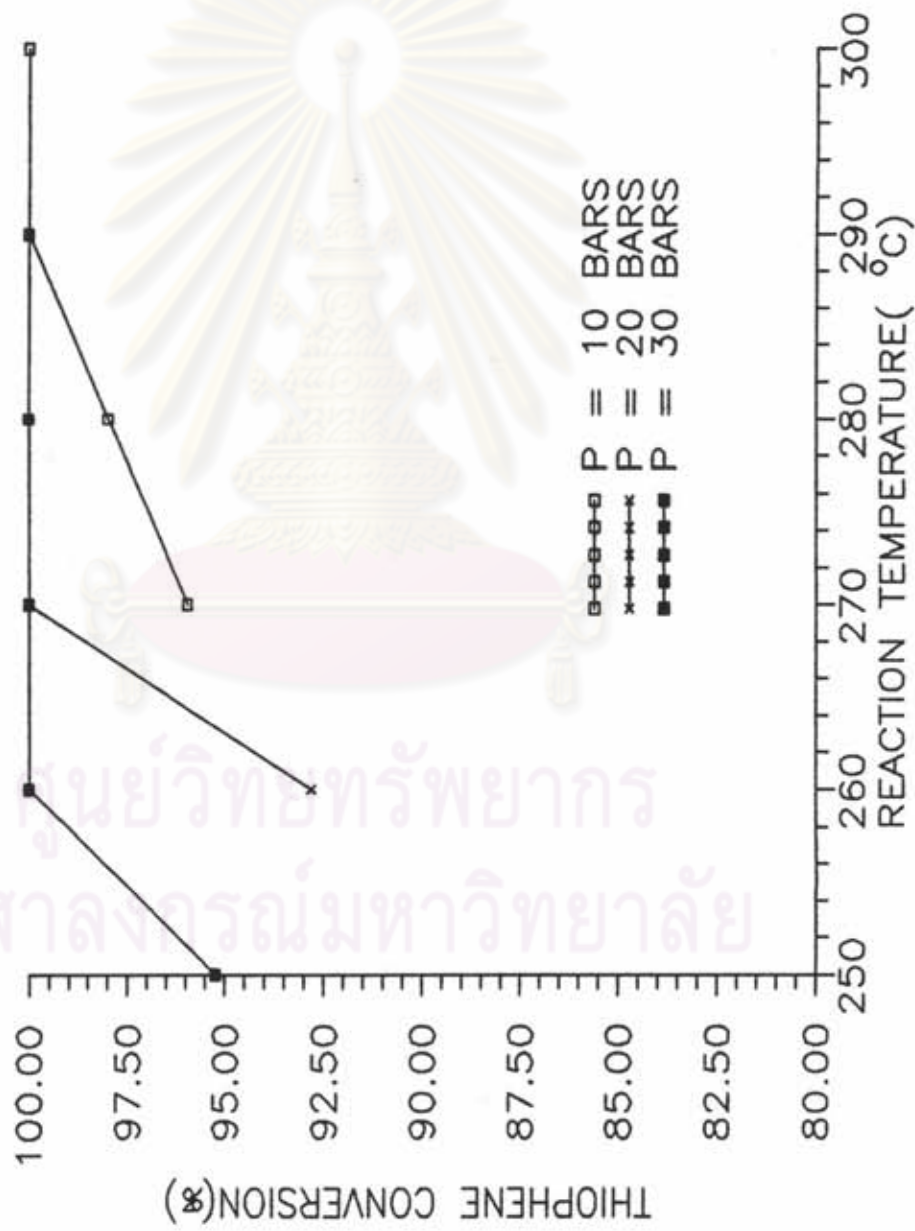
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TABLE 4.11 THIOPHENE CONVERSION AFTER 10 HOURS AS FUNCTION OF TEMPERATURE AT LHSV = 6 HR<sup>-1</sup>

TEMP. (°C)	P = 10 BARS	P = 20 BARS	P = 30 BARS
	CONVERSION (%)	CONVERSION (%)	CONVERSION (%)
240			88.05
250			95.44
260			100.00
270		98.43	100.00
280		100.00	
290		100.00	
300	97.70	100.00	
310	97.83		
320	96.60		
330	100.00		

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FIGURE 4.8 THIOPHENE CONVERSION VS REACTION TEMPERATURE  
AT LHSV = 2.6 HR<sup>-1</sup>

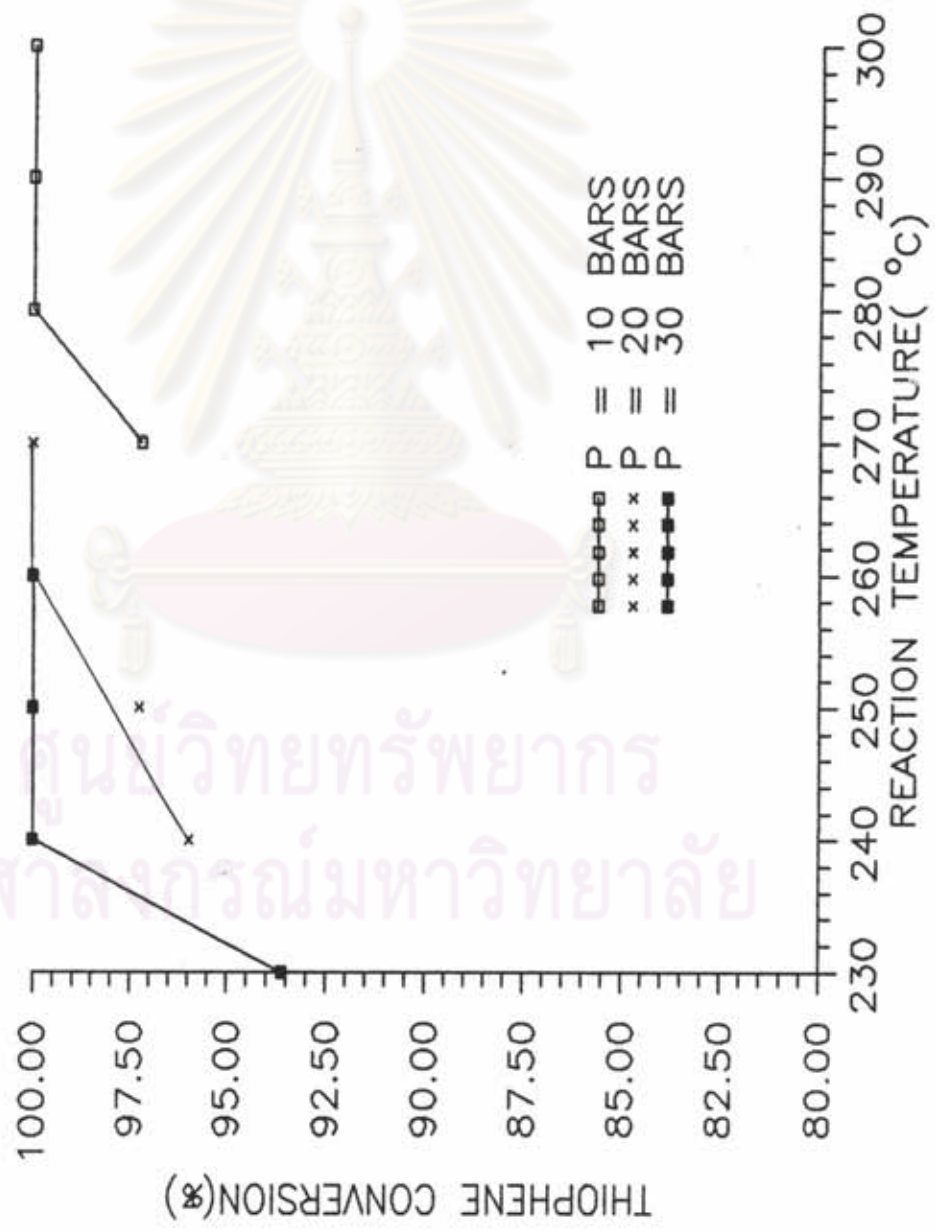


FIGURE 4.9 THIOPHENE CONVERSION VS REACTION TEMPERATURE AT LHSV = 4 HR<sup>-1</sup>

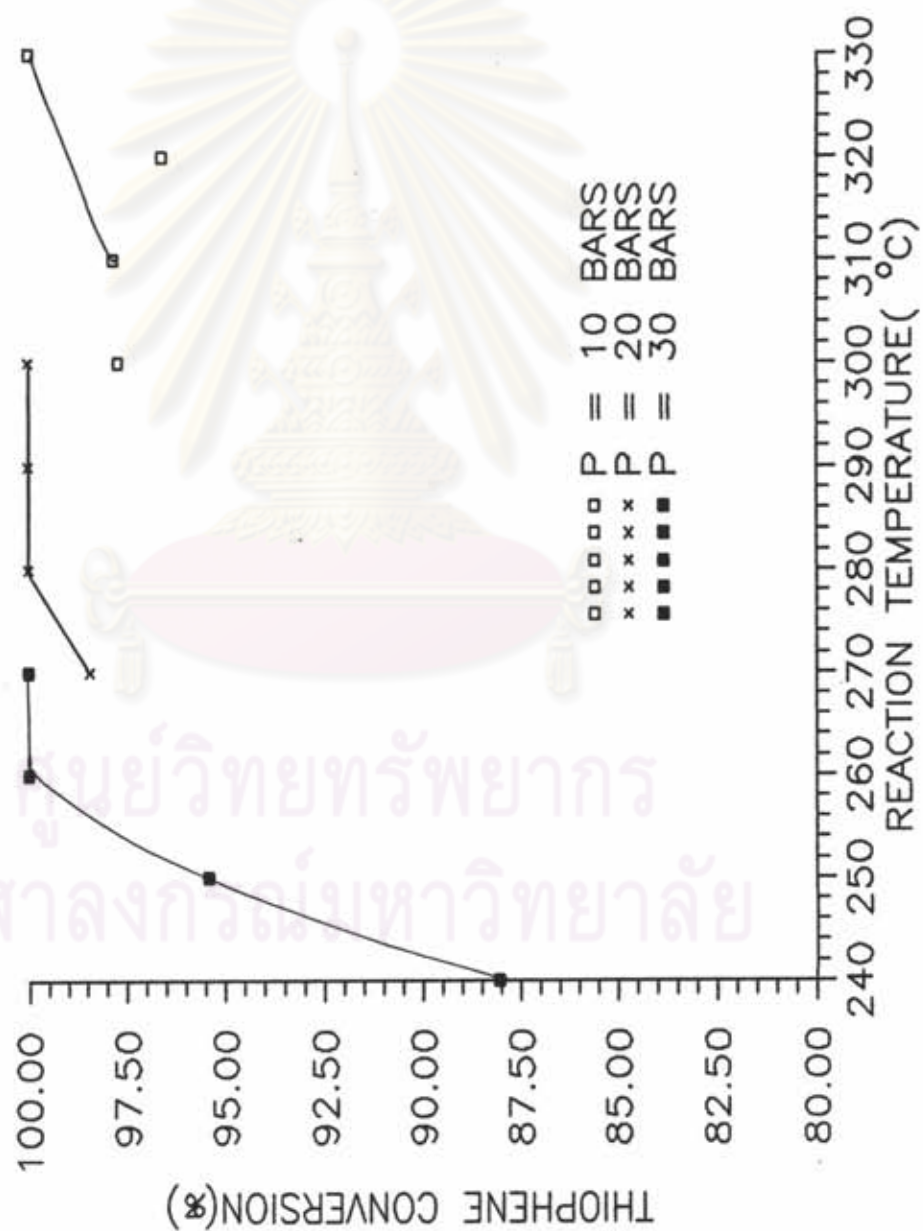


FIGURE 4.10 THIOPHENE CONVERSION VS REACTION TEMPERATURE AT LHSV = 6 HR<sup>-1</sup>

#### 4.2.4 Application of observed optimum conditions

In the previous sections, the optimum conditions for deep hydrodesulfurization of toluene containing thiophene were concluded to be:

total pressure = 30 bars and LHSV = 4 hr<sup>-1</sup>

To confirm the high removal efficiency at a much higher thiophene feed concentration, the obtained optimum conditions were applied to desulfurize 1 wt% (10,000 ppm) thiophene in toluene. As shown in Table 4.12 and Figure 4.11, complete removal of thiophene could still be achieved at 310 °C using catalyst SELF-2 at 30 bars and LHSV = 4 hr<sup>-1</sup>.



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TABLE 4.12 THIOPHENE CONVERSION AS FUNCTION OF REACTION TIME AT VARIOUS TEMPERATURES FOR SELF-2 CATALYST AT P=30 BARS LHSV= 4 HR<sup>-1</sup>

TIMES (HOURS)	TEMP.= 300 °C		TEMP.=320 °C		TEMP.= 310 °C		TEMP.= 290 °C		TEMP.= 310 °C (REPEAT)	
	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)	CONC. (ppm.)	CONVERSION (%)
0.00	10000.00	0.00	0.00	0.00	10000.00	0.00	10000.00	0.00	10000.00	0.00
0.50	153.92	98.46	103.24	98.97	0.00	100.00	292.49	97.08	0.00	100.00
2.00	11.22	99.89	0.00	100.00	0.00	100.00	72.29	99.28	0.00	100.00
4.00	9.19	100.00	0.00	100.00	0.00	100.00	51.05	99.49	0.00	100.00
6.00	0.00	100.00	0.00	100.00	0.00	100.00	51.84	99.48	0.00	100.00
8.00	0.00	100.00	0.00	100.00	0.00	100.00	28.18	99.72	0.00	100.00
10.00	0.00	100.00	0.00	100.00	0.00	100.00	27.46	99.73	0.00	100.00

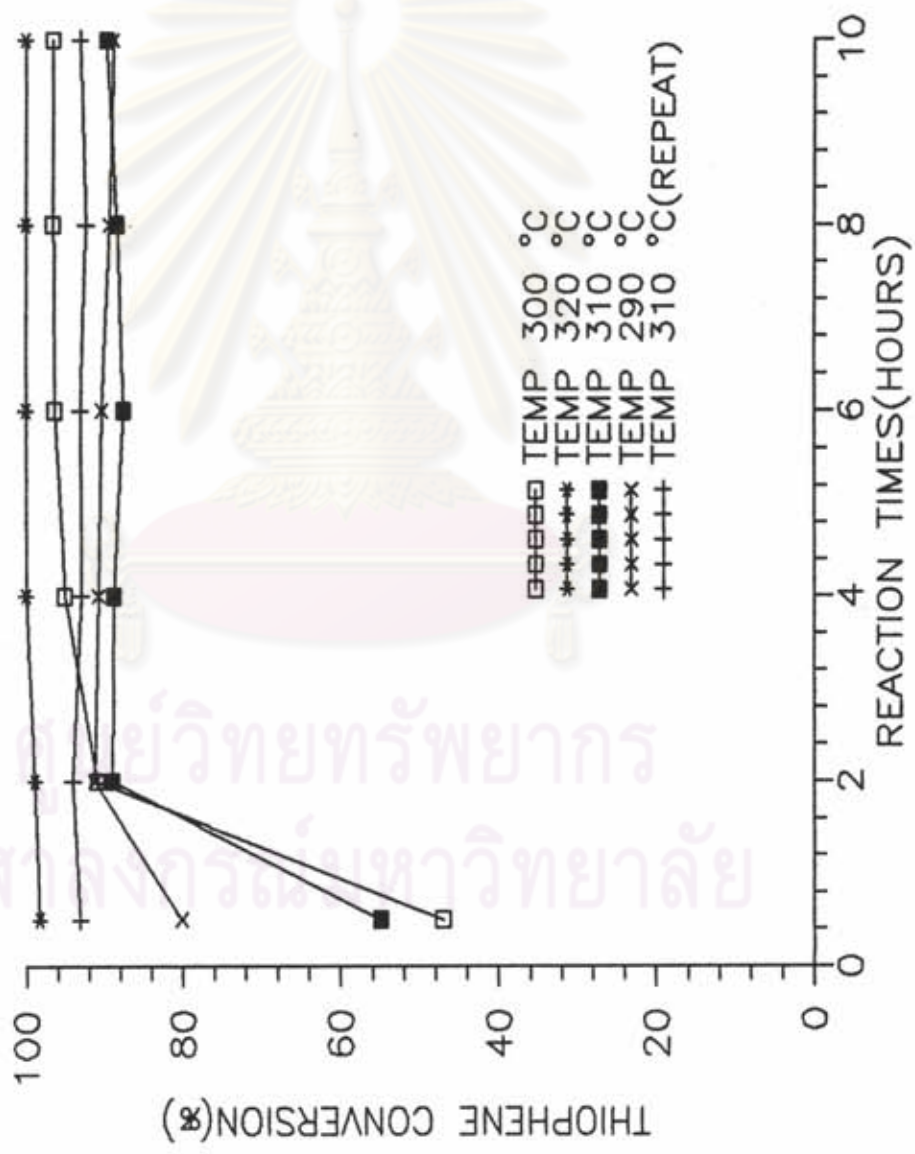


FIGURE 4.11 THIOPHENE CONVERSION VS REACTION TIMES OF 1 wt% THIOPHENE IN TOLUENE AS FEED

### 4.3 The presulfiding (activation) process

Presulfiding (activation) of the catalyst used in this study was mainly done by the sulfur(thiophene) in the feed (about 1 wt% S on feedstock). Specifically this study used toluene containing 1 wt% thiophene as sulfiding agent. The outlet concentration of thiophene was observed after feeding the sulfiding agent to the catalyst and the reaction temperature was increased from 150 °C to 300 °C at constant rate.

The results of the presulfidation are summarized in Table 4.13. As shown graphically in Fig. 4.12, the amount of thiophene remaining at the outlet dropped and reached a steady value as the presulfiding time increased. During presulfidation the sulfur compounds (thiophene) decomposed to H<sub>2</sub>S that subsequently reacted to change cobalt oxide and molybdenum oxide into cobalt sulfide and molybdenum sulfide (the active species).

The presulfiding process was assumed completed when the outlet concentration of thiophene remained constant. We found that the concentration of thiophene at the outlet after the completion of presulfidation was related to the catalytic activity of the three catalysts. In short at 270 °C, SELF-2 catalyst could completely remove thiophene after 4 hours, while TOC-CAT and SELF-1 catalyst could remove only 96.62 and 96.50% after 10 hrs (see Tables 4.2 - 4.4). In other words, the lower the steady outlet concentration of thiophene, the higher the consumption of thiophene used to presulfide the catalyst, and the more active the catalyst.

TABLE 4.13 THIOPHENE CONCENTRATION AS FUNCTION  
PRESULFIDING TIME

TIMES (HOURS)	TOC-CAT	SELF-1 CAT	SELF-2 CAT
	CONC. (wt %)	CONC. (wt %)	CONC. (wt %)
0.00	1.27	1.82	1.82
0.50	1.13	1.70	1.69
1.00	1.11	1.67	1.68
1.50	1.11	1.56	1.63
2.00	0.99	0.92	0.57
2.50	0.74	0.99	0.56
3.00	0.77	1.07	0.38
3.50	0.77	1.09	0.41
4.00	0.80	1.10	0.45

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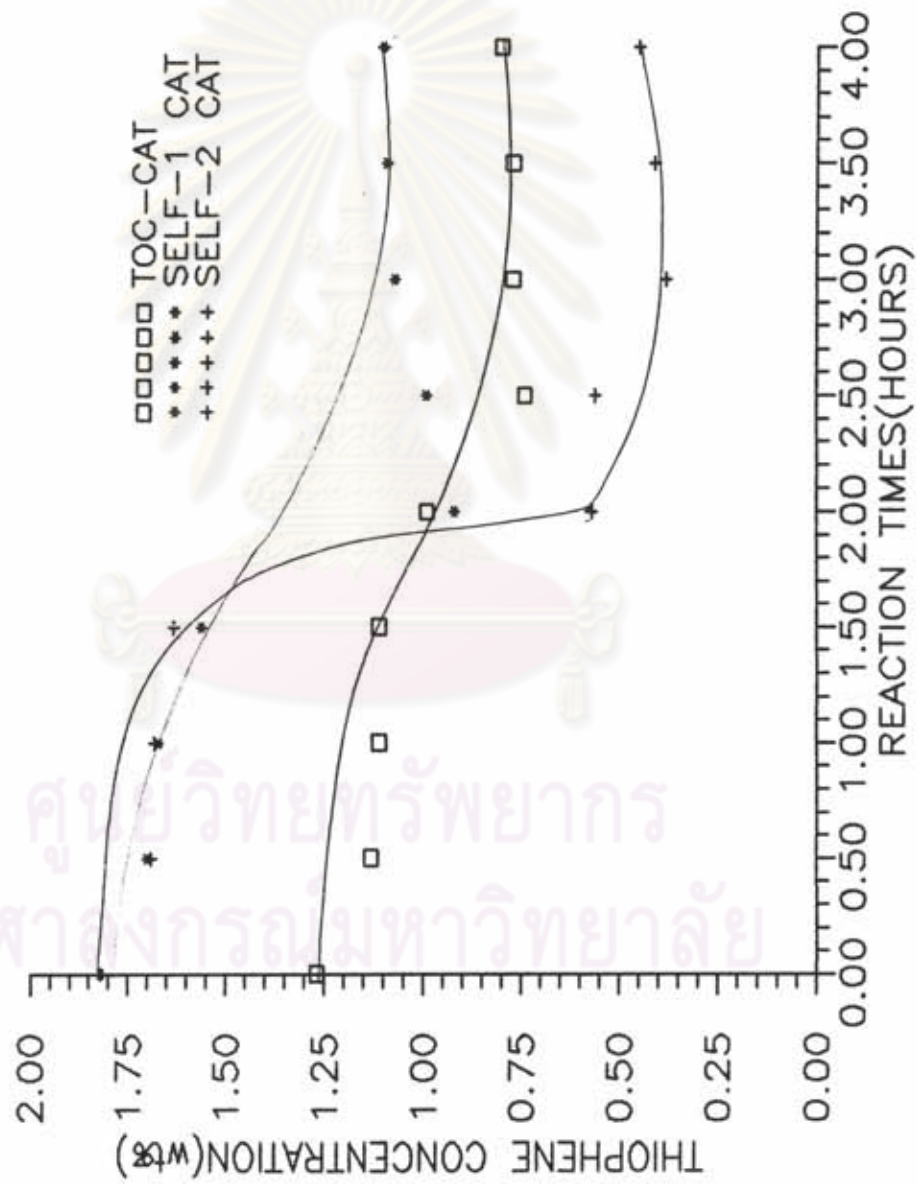


FIGURE 4.12 THIOPHENE CONCENTRATION VS PRESULFIDING TIME

## CHAPTER 5

### CONCLUSIONS AND FURTHER STUDY

The following conclusions may be drawn from the present work

1. The SELF-2 catalyst is the most active catalyst among the three catalysts used in hydrodesulfurizing a synthetic feed of toluene containing thiophene about 500 ppm. Thus this catalyst has been studied in further details.

2. The following study was carried out to investigate the effects of reaction conditions :

Toluene containing thiophene about 500-600 ppm as feed

Total pressure = 10,20,30 bars

Molar ratio of hydrogen to feed = 10:1

Liquid hourly space velocity = 2.6,4,6 hr<sup>-1</sup>

The temperature of each experiment was varied to find the minimum temperature that deep hydrodesulfurization was observed. It may be concluded that the effects of temperature, pressure, space velocity were as follows:

2.1 The higher the pressure, the higher the removal efficiency of thiophene. The optimum pressure observed was 30 bars.

2.2 The observed optimum liquid hourly space velocity for severe hydrodesulfuration was  $4 \text{ hr}^{-1}$ .

2.3 The higher the temperature, the higher the thiophene removal efficiency.

3. The chosen method for presulfidation involved the use of about 1 wt% thiophene in the normal feedstock to activate the catalyst. The required presulfiding time was about 4 hours after feeding the sulfiding agent to the catalyst and the reaction temperature was increased from  $150^\circ\text{C}$  to  $300^\circ\text{C}$  at a constant rate.

#### FUTHER STUDY

For further study, we might study the hydrodesulfurization of straight-run light oils while using the selected catalyst presulfiding process and reaction conditions obtained in this work. One necessary modification is to change the separation column of the gas chromatography which is equipped with a flame photometric detector (FPD) from a 2.6 mm O.D. glass packed with carbopack BHT 100 to a 50-meter-long capillary column in order to separate and analyze the hydrodesulfurization and hydrocarbon products with boiling points above  $120^\circ\text{C}$ . The maximum allowable temperature of the present carbopack BHT 100 column was only  $150^\circ\text{C}$ .