CHAPTER III

EXPERIMENT AND ANALYSIS TECHNIQUES

Experimental Apparatus

The study of hydrodesulfurization of thiophene was conducted in a fixed-bed reactor system as shown in Figure 3.1. The experimental reactor is described in detail elsewhere [Tanpichart, 1992 and Chantalakka, 1993]. In this study, the reactor is 48 cm. (18.90 inch) long, 1.27 cm. (0.5 inch) outside diameter, 0.089 cm. (0.035 inch) thick, and 316 stainless steel tube.

Experimental Procedures

The commercial catalysts used in this study were $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$, which donated by Bangchark Company Limited. All experiments described here with hydrodesulfurization of thiophene were performed in a fixed-bed reactor at a total pressure of 400 psig and temperatures ranging from 240-260°C. Hydrogen was fed at a rate of 400 cc/min and a weight hourly space velocity of 3.0 hr^{-1}. A solution containing 3 wt% of thiophene in toluene was introduced into the reactor during 144 hours. For deactivation experiment, the solution was replaced by a solution containing 3 wt% of thiophene and 0.5 wt% of quinoline after 48 hours and 96 hours. Liquid products

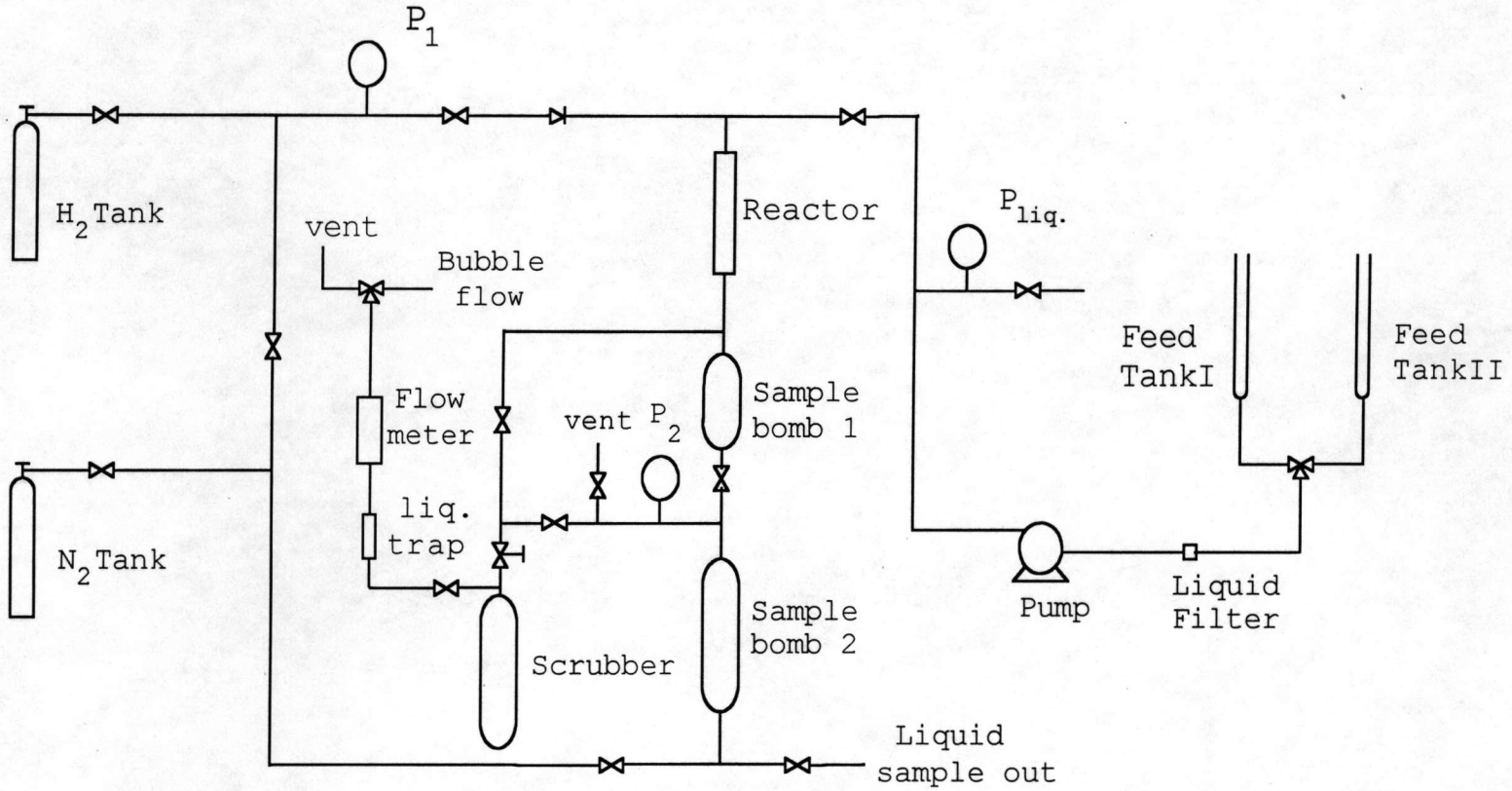


Figure 3.1 Simplified Diagram of Hydrodesulfurization System

were withdrawn every 6 hours during each experiment and analyzed by a FID gas chromatograph. Table 3.1 summarizes the experimental operating conditions of hydrodesulfurization of thiophene.

Table 3.1 The Experimental Operating Conditions

Reactor Temperature, °C	: 240, 250, 260
Pressure, psig	: 400
WHSV, hr^{-1}	: 3.0
Liquid Flow Rate, cc/hr	: 10
H_2 : Oil Ratio	: 2400 : 1
Hydrogen Flow Rate, cc/min	: 400
Reaction Time, hrs.	: 144
Sampling Time, hrs.	: 6
Catalyst	: Extruded of $CoMo/Al_2O_3$
	Extruded of $NiMo/Al_2O_3$
Catalyst Weight, g.	: 3.0

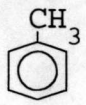
Properties of the chemicals used in these experiments are given in Table 3.2 to 3.5, respectively.

Table 3.2 Properties of Thiophene*

Formula	C_4H_4S
Structure	
Chemical name	Thiophene
Physical properties	
Molecular weight	84.14
Form	liquid
Color	colorless
Melting point (°C)	-38.2
Boiling point (°C)	82-84
Specific gravity	1.063
Solubility	Soluble in alcohol, ether, acetone, benzene
Purity	> 98%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and Supplier

Table 3.3 Properties of Toluene*

Formula	C_7H_8
Structure	
Chemical name	Toluene
Physical properties	
Molecular weight	92.14
Form	liquid
Color	colorless
Melting point (°C)	-95
Boiling point (°C)	110.8
Specific gravity	0.87
Solubility	Soluble in ether and alcohol
Purity	> 99.5%
Supplier	Merck

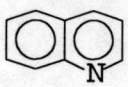
* From Encyclopedia of Chemical Engineering and Supplier

Table 3.4 Properties of Hexanes*

Formula	C_6H_{14}
Structure	$CH_3CH_2CH_2CH_2CH_2CH_3$
Chemical name	Hexanes
Physical properties	
Molecular weight	86.18
Form	liquid
Color	colorless
Melting point (°C)	-94
Boiling point (°C)	68.7
Specific gravity	0.663
Solubility	Soluble in alcohol, ether, benzene
Purity	99.7%
Supplier	J.T. Baker Inc.

* From Encyclopedia of Chemical Engineering and Supplier

Table 3.5 Properties of Quinoline*

Formula	C_9H_7N
Structure	
Chemical name	Quinoline
Physical properties	
Molecular weight	129.16
Form	liquid
Color	Brown-Black
Melting point (°C)	-17 to -13
Boiling point (°C)	108-110
Specific gravity	1.093
Solubility	Soluble in alcohol and ether
Purity	> 97%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and Supplier

Analysis Techniques

After each experiment, liquid samples were analyzed for concentration of each compound. Liquid samples of the reactor effluent were collected downstream of the phase separator, and concentrations were related to the starting liquid feed. Reaction samples were analyzed by Shimadzu GC-8APF gas chromatograph, using a 50 m OV-1 Bonded capillary column (GL Sciences Inc.). Approximate 0.3 microliter of liquid sample was injected into gas chromatograph. The sample was vaporized at a high temperature and mixed with a carrier gas. Part of the gas mixture was spilt and vented to the atmosphere, only a small portion of the gas mixture flowed into the capillary column. Compounds (thiophene, hexane, toluene, quinoline, and their hydrogenated products) in the gas mixture were adsorbed and desorbed in capillary column at different rates. Lighter compounds were adsorbed and desorbed faster than heavier compounds. The gas mixture flowed through a tip where the compounds were burned in a hydrogen flame. Flame ionization detector was used to detect signal. The signal was plotted and integrated by the Shimadzu C-R6A Chromatopac. The operating conditions of the gas chromatograph are summarized in Table 3.6.

Qualitative analysis of the samples was obtained from retention times. The compounds were identified by comparing the retention times of the unknown peaks with the retention times of standard compounds. The standard retention times were measured in the laboratory using the

same gas chromatograph and operating conditions. The retention times of the standard compounds suspected to be in the liquid samples are shown in Table 3.7.

Quantitative analysis of the chromatograms was obtained by electronic integration of the peak areas. Response factors were obtained by integration of chromatograms of known quantities of compounds.

Table 3.6 Column Conditions

Initial temperature	60	°C
Initial time	15	minutes
Final temperature	170	°C
Final time	15	minutes
Injector temperature	200	°C
Detector temperature	200	°C

Table 3.7 Retention Times

Compounds	Retention Time (min.)
n-Hexane	3.61
Thiophene	4.22
Toluene	7.38
Quinoline	32.74