CHAPTER III

EXPERIMENTAL APPARATUS AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus.

In this study, a fixed-bed flow reactor system is used for hydrodesulfurization of thiophene. This system was designed and used by earlier investigators at Chulalongkorn University. Modification of some parts was made in this study. The system was designed and constructed in order to withstand a maximum operating temperature of 350°C (662°F) and a maximum operating pressure of 1600 psig (11.03 MPa). Stainless steel tubes, fittings and valves were used to protect the system from corrosion. A schematic diagram of the system is shown in Figure 3.1.

Gas and liquid feed flow into the top of fixed-bed flow reactor from two separated sections, called gas section and liquid section. In the gas section, hydrogen gas is fed to by-pass valve 17 and 18 through a mass flow meter to measure upstream hydrogen gas flow rate before going to the top of the reactor. Mass flow meter is Allborg Instrument Model AFM-2600 having a capability to be used for maximum pressure of 500 psig (3.447 MPa).

Nitrogen gas is fed through valve 16 into the top of the reactor. In the liquid section, each feed is filled in a burette (feed tank which shows liquid level) and is pumped through valve 1 and liquid filter into Eldex Precision Metering Pump which has ability to

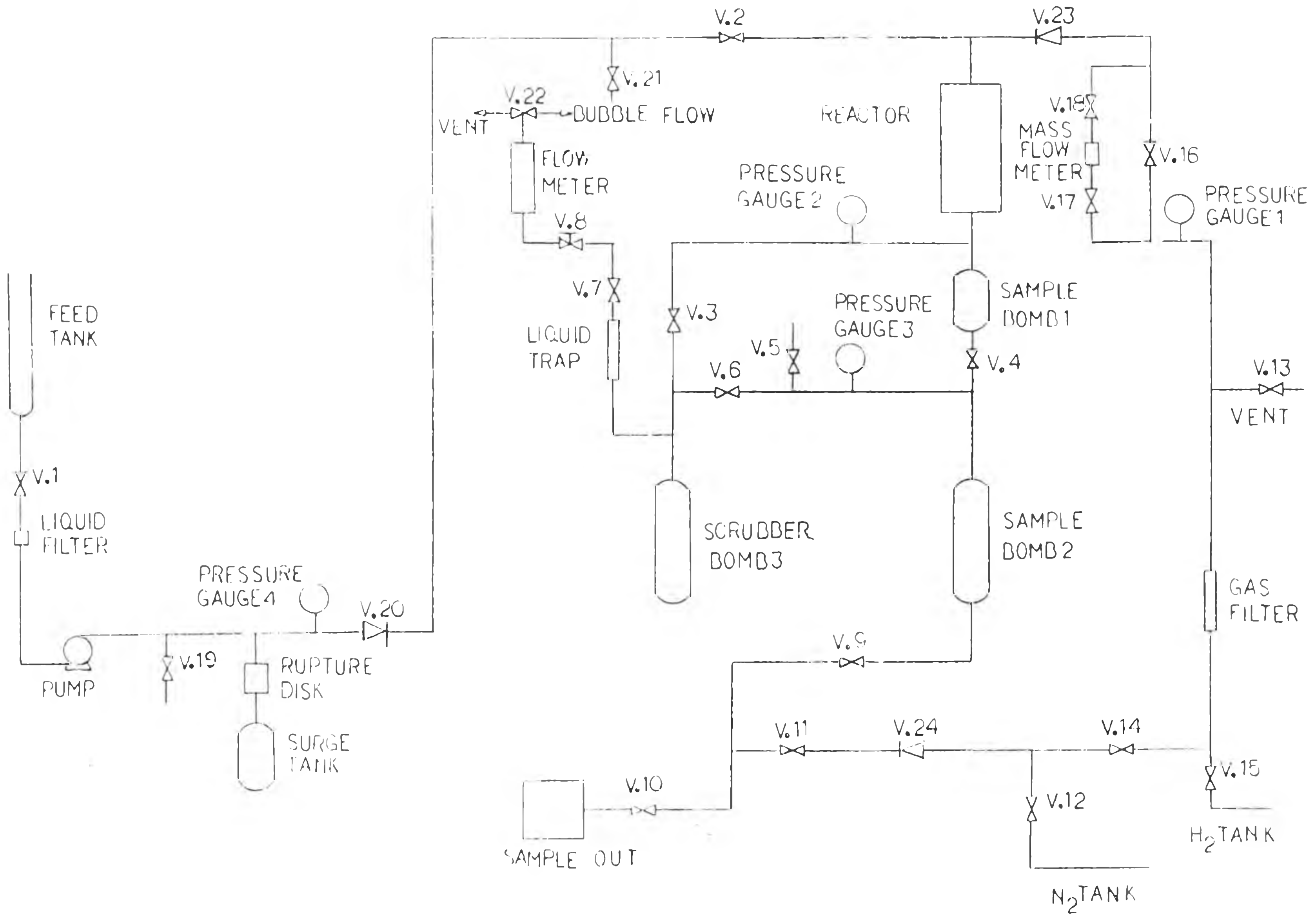

FIGURE 3.1 A SCHEMETRIC DIAGRAM OF THE SYSTEM

generate high pressure at low flow rate. The feed pressure is monitored by pressure gauge 4 located upstream from check valve 20. Safety line located before pressure gauge 4 is equipped with rupture disk, rated at 2000 psig (13.8 MPa) and surge tank is used to protect feed system from excessive pressure. Feeds and hydrogen gas flow concurrently downward through reactor which is packed in the middle part with 3 grams of catalyst supported by glass beads. The reactor consists of a 17 inch (43.2 cm.) long, 0.5 inch (1.27 cm.) outside diameter, and 0.035 inch (0.089 cm.) thick, 316 stainless steel tube. A 1/2-inch Swagelok cross is connected to the top of the reactor. Two 1/2-inch to 1/4-inch reducers are connected to both sides of cross joined with liquid and gas lines, respectively. A 1/8-inch outside diameter, 316 stainless steel tube, with one end welded shut is used as a thermowell. The thermowell is secured in the middle of the reactor by means of a 1/4-inch to 1/8-inch reducing union which is drilled for inserting the thermowell. A small thermocouple is inserted into the thermowell to measure the temperature of the catalyst bed during the reaction.

Two iron blocks, with grooves of reactor diameter running across their entire length are used as the heating blocks. The heating blocks are made to be fitted with heating bands which are placed around the assembled blocks. Two heating bands, rated at 800 watt and 220 volt are used to supply heat for the reactor. Fiberglass is also wrapped around the reactor as insulator to keep system isothermal and protect personnel from hot surface. Two thermocouple are placed outside the reactor wall, one for measurement of temperature at outside reactor wall and the other for the temperature programmer/controller.

The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer to enable it to be connected to the sampling system.

Product oil and gas flow through sample bomb 1 into the sample bomb 2 where they are separated. Upstream pressure of the system is monitored by pressure gauge 1. Downstream pressure of the system is monitored by pressure gauge 2 and 3, which are connected to sample bomb 1 and sample bomb 2, respectively. The upstream pressure is considered as the reactor or system pressure. The gas flow rate is maintained by means of micrometering valve 8. The gas flow is monitored and controlled dowstream from the micrometering valve by a low pressure rotameter and a bubble flow meter, respectively.

A scrubber filled with sodium solution (60 vol% sodium hydroxide in water) is located after valve [illegible]. Liquid trap is used to prevent liquid and particle flowing into the gas measuring devices.

The liquid products are withdrawn every 6 hours during each experiment without interruption to the system by closing valve 6 and 4. Liquid product generated during sampling process is accumulated in sample bomb 1 while gaseous products flow through valve 3 into scrubber unit before venting to atmosphere. At sample bomb 2, there was both liquid and gaseous products which are withdrawn after 6 hours. Only gaseous products are vented to the outdoor scrubber unit through valve 5 while liquid products are collected into liquid sample box through valve 9 and 10. After finishing sampling process, change the system to steady state by pressurizing sample bomb 2 with nitrogen gas about 350 psig (2.41 MPa) through valve 12, 24, 11 and 9, respectively before closing valve 9, 3 and slowly opening valve 4 and valve 6, respectively. After each experiment,liquid products and used catalysts are labeled and kept for analysis.

3.2 Analysis Techniques

After each experiments, liquid samples were analyzed every 12 hours for concentration of each compounds. Fresh and spent catalysts samples were analyzed for coke and their characteristic.

3.2.1 Product Characterization

Gas Chromatographic Analysis of liquid products: A Perkin Elmer Model 8700 Gas Chromatograph equipped with GL Science Capillary Column Model OV-1 is used to determine the amount of thiophene, n-hexane, toluene and their hydrotreating products in the liquid samples. About 0.5 microliter of liquid sample is injected with 1/8 split ratio. The sample is vaporized at a high temperature and mixed with a carrier gas. Compounds in the gas mixture adsorp and desorp in the capillary column at different rates. Lighter compounds adsorb and desorb faster than heavier compounds.

Flame ionization detector is used to detect the signal. The signal are plotted and integrated. Then they are printed on an Epson FX 850 dot matric printer.

The operating conditions of the gas chromatograph are summarized in Table 3.1.

Qualitative analysis: The compounds are identified by comparing the reaction times of the unknown peaks with the reaction times of standard compounds suspected to be in the samples. The standard retention time were measured in laboratory using the same chromatograph and operating conditions.

Quantitative analysis: The results obtained from the gas chromatograph were used to determine composition of the samples. The integrated area shown on the chromatogram were used to calculate concentrations of compounds in the solution.

3.2.2 Catalyst Characterization

Samples of fresh and spent catalysts from each experiment were extracted with tetrahydrofuran in a Soxhlet Extraction unit for 6 hours. Extracted catalysts were dried at room temperature for 12 hours. Then the extracted fresh and spent catalysts were divided in two groups. First group was regenerated in the furnace to determine coke content and the catalyst samples after determination for coke content are called burned catalysts. Second group was not regenerated in the furnace and the catalyst samples from this group are called unburned catalysts. Fresh and spent catalyst samples from both groups were analyzed for pore characteristic and total surface area.

TABLE 3.1 Column Conditions

Operating Conditions	Feed I	Feed II
Initial Temperature (°C)	27	32
Isotime I (min)	27	32
Heating Rate (°C/min)	-	6
Final Temperature (°C)	27	150
Isotime II (min)	-	10
Injection Temperature (°C)	170	200
Detector Temperature (°C)	170	200

TABLE 3.2 Retention Times

Compounds	Feed I	Feed II
n-Hexane	5.9	5.43
Thiophene	7.85	7.07
Toluene	16.75	14.22
Pyridine	12.33	12.80
Quinoline	-	46.82
1,2,3,4-Tetrahydroquinoline	-	46.50
2,6-Lutidine	-	27.66
Pyrrole	12.30	12.05

(a) Coke Content Characterization

The coke content in this study is defined as the weight percent of loss of carbonaceous material by burning the catalyst sample at 550°C (1022°F) for 60 hours. The catalyst samples are weighed at room temperature and placed in a furnace at 550°C (1022°F) to burn off their carbonaceous material for 60 hours. The samples are allowed to cool down to room temperature then weighed. The amount of coke is calculated by :

$$\text{Weight\% of coke content} = (W_1 - W_2) * (100/W_1)$$

Where W_1 = Weight of spent catalyst

W_2 = Weight of burned catalyst

(b) Catalyst Characteristic.

Fresh and spent catalysts were classified in two groups called burned and unburned catalyst. These catalysts were analyzed for pore charateristic and total surface area.

(c) Pore characteristic

A micromeritics model 9320 Poresizer was used to determine the pore volume and pore area. This analyzer used mercury penetration method. This method is based on the behavior of nonwetting liquids in capillaries, again usually assuming that pores can be represented as cylinders. This analyzer has two operating steps. The first step is a low pressure process in which nitrogen gas at 25 psig was gradually increased to force mercury to penetrate into the pore of catalyst. The second step is high pressure process in which oil was used for hydraulic pressurization. Step increase in pressurization was assigned by any users, called pressure table which memoried in computer program. The maximum and the minimum operating pressure of high pressure process are 25 and 28,000 psig which is adequate to force mercury to penetrate into the pore of catalyst. Total data from both steps are combined to calculate the pore volume.

(d) Total surface area

A micromeritics model ASAP 2000 was used to determine the total surface area of catalysts. There are two operating step, the degassing step and analysis step.

Most solid materials adsorb moisture and other contaminants when exposed to the atmosphere. The sample must be clean when analysis is performed. The sample is heated and placed under vacuum to remove the moisture and other contaminants. Before taking catalyst sample to the degas port, it is good practice to dry sample prior to treat them in the degas stations. A vacuum oven was used in this treatment and carried out at 170°C and vacuum pressure of 1 inch of Hg for 5 hours. At the degas port, the condition is fast vacuum to 500 m Hg at 250°C for 3 hours. After completion of this step, the catalyst was weighed and, then the degased sample was transfer from the degas port to the analysis port.

At the analysis port, before a sample can be automatically analyzed it must have an information file assigned to it. The file consists of information groups which collectively, identify the sample (sample information), guide the analysis (run conditions, pressure table) and specify the data reduction (calculation assignments, report options).

Analysis of samples were carried out at vacuum pressure of 15 mmHg and cold dewar filled with liquid nitrogen to generate nitrogen adsorption. Amount of nitrogen adsorption related with setting of P/P_0 (P = pressure and P_0 = saturated pressure) at 0.3 called one point adsorption, was chosen to calculated the total surface area.