

CHAPTER III

EXPERIMENTAL APPARATUS AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

In this study, a trickle bed reactor system is used for hydrodesulfurization (HDS) of thiophene. 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 feeds flow into the trickle bed reactor from two separate sections, called gas section and liquid section. In gas section, hydrogen is fed through valve 1 and valve 4 into the top of the reactor. Inlet gas pressure is measured by pressure gauge 1 which is located between valve 1 and valve 4. Hydrogen pressure is controlled by a pressure regulator at the hydrogen cylinder. Feed oil is filled into the feed tank and is pumped through valve 11 into Eldex precision metering pump. From the metering pump, the feed oil is charged through valve 12 and valve 13 into the reactor. The pressure in liquid section is monitored by pressure gauge 4 located upstream from valve 12. Oil and hydrogen gas flow concurrently through the reactor, which is packed in the middle part with 10 grams of

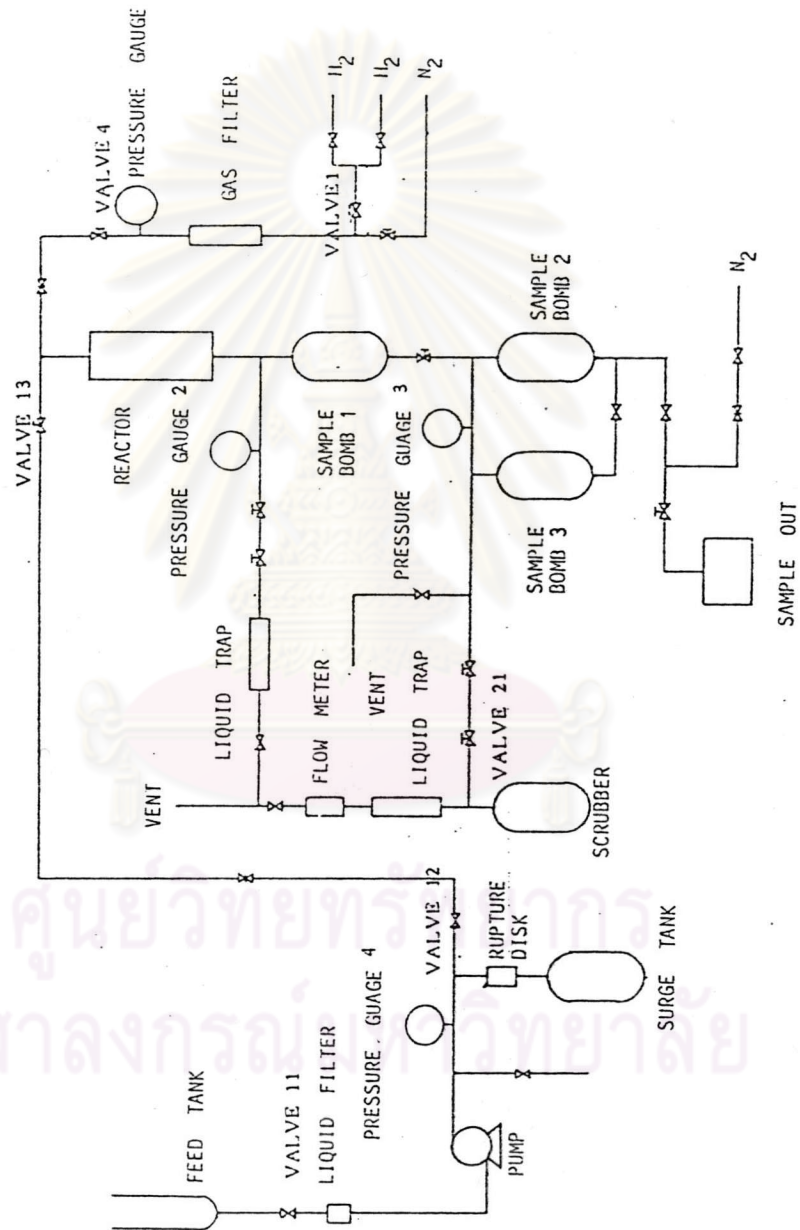


Figure 3.1 A Schematic Diagram of the System

catalyst supported by glass beads. The reactor is made of a 43.2 cm (17 inches) long, 1.27 cm (0.5 inch) outside diameter, and 0.089 cm (0.035 inch) thick, 316 stainless steel tube. A 0.317 cm (0.125 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. A small thermocouple is inserted into the thermowell to measure the temperature of the catalyst bed during the reaction. Another thermocouple is placed outside the reactor wall to measure the temperature of the reactor. This temperature is used to control the reactor temperature. Two heating bands are used to generate heat for the reactor. An insulating material is wrapped around the heating bands to prevent heat loss and to protect personnel from hot surface.

Product oil and gas flow through sample bomb 1 into sample bomb 2 where they are separated. The pressure of sample bomb 1 is used as the reactor downstream pressure and is measured by pressure gauge 2. The pressure of sample bomb 2 is measured by pressure gauge 3. Sample bomb 3 is used to further condense the liquid product.

The outlet gas stream flows into a scrubber which is filled with ethanolamine solution (67 vol% ethanolamine in water) and is located downstream from valve 21. The outlet gas flow rate is controlled by valve 21, a micro-metering valve. A bubble flow meter and a low pressure flow meter are used to measure and monitor the gas flow rate.

The liquid products were taken every 6 hours during

each experiment. After each experiment, the catalyst in the reactor was divided into three sections called top, middle and bottom. Each oil sample and catalyst sample were labeled and kept for analyses.

3.2 Analysis Techniques

After each experiment, spent catalyst samples were analyzed for coke content and metal distribution. Liquid samples were analyzed for concentration of each compound and metal contents.

3.2.1 Catalyst Characterization

Each catalyst sample was extracted with tetrahydrofuran in a Soxhlet extraction unit for 6 hours. The washed catalysts were dried at room temperature for 12 hours. Then the catalyst sample were analyzed for coke content and metal distribution.

Coke Content determination: 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

Metal distribution determination: A JEOL Model JSM-T220A Scanning Electron Microscope equipped with a LINK Model EDX 860 Energy Dispersive X-ray Analyzer is used to determine the metal distribution in spent catalysts. A catalyst pellet in each section is cut cross-sectionally and placed in a vacuum chamber. The metals in the catalyst are analyzed by the X-ray beam of different energies. The catalyst samples are analyzed at four locations from the edge to the center of the pellets, as shown in Figure 3.2.

3.2.2 Product Characterization

Gas Chromatographic Analysis of liquid products: A Perkin Elmer Model 8700 Gas Chromatograph equipped with Gl Sciences capillary column Model OV-1 is used to determine the amount of thiophene, toluene and their hydrotreating products in the liquid samples. Approximately 0.5 microliter of liquid sample is injected into the Gas Chromatograph. The sample is vaporized at a high temperature and mixed with a carrier gas. Part of the gas mixture is split and vented to the atmosphere, only a small portion of the gas mixture flows into the capillary column. Compounds in the gas mixture adsorb and desorb in the capillary column at different rates. Lighter compounds adsorb and desorb faster than heavier compounds. The desorbed gas is added to the make up gas to increase the gas flow rate. The gas mixture flows through a tip where the compounds are burned in a hydrogen flame. Flame Ionization Detector is used to detect the signal. The signals are plotted and integrated. Then they are printed on an Epson FX 850 dot matrix printer. The

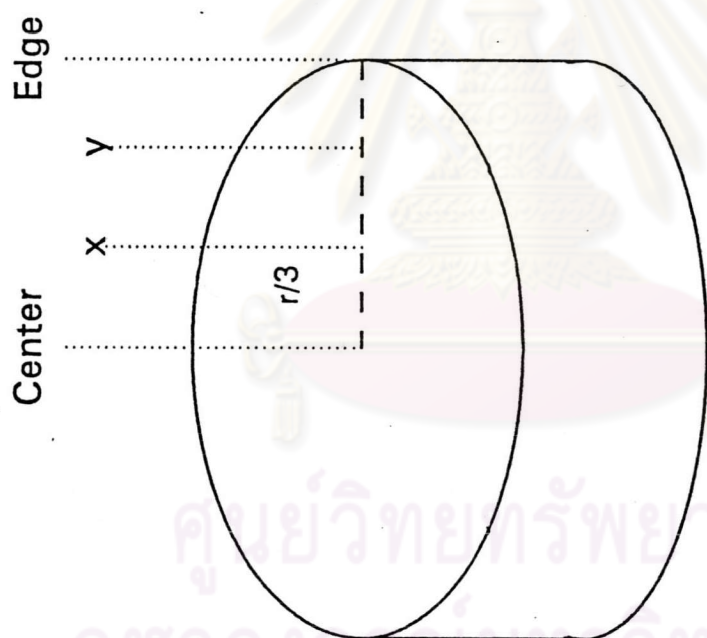


Figure 3.2 Cross-Section of the Catalyst Pellet

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

Qualitative analysis: The compounds are identified by comparing the retention times of the unknown peaks with the retention times of standard compounds. Table 3.2 shows the retention times of standard compounds suspected to be in the samples. The standard retention times were measured in our laboratory using the same gas chromatograph and operating conditions.

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

Metals Concentrations Determination: A Instrumentation Laboratory Model IL 551 Atomic Absorption and Atomic Emission Spectrometers is used to measure the metals concentrations in the feedstock and product oils.

Atomic adsorption is a chemical analysis technique which uses light absorption by atoms in the gas phase to analyze the metal atoms. It is used to analyze metal samples in solutions in the range of parts-permillion (ppm). Although it is very sensitive and quantitative technique, it can treat only one element at a time.

In atomic absorption spectroscopy, a solution of the sample is introduced into a chemical flame as a fine aerosol or mist. Here the solution droplets first undergo desolvation and the resulting particles are dissociated into atoms.

TABLE 3.1 Column Conditions

Initial Temperature	30°C
Initial Time	10 minutes
Heating Rate	5°C/min
Final Temperature	80°C
Final Time	35 minutes
Injector Temperature	170°C
Detector Temperature	170°C

TABLE 3.2 Retention Time

Compounds	Retention Time (min.)
Benzene	7.25
Thiophene	7.45
Cyclohexane	7.70
Methylcyclohexane	11.25
Toluene	13.95

These atoms are in their normal electronic configuration, the "ground state" or zero energy state. An external light source is employed to emit the atomic line spectrum of the atom to be analyzed. The light from this source passes through the flame containing the sample and is absorbed by the ground state atoms in the flame cell. The photons emitted by the element in the external source have exactly the energy required to excite the same ground state element in the flame. The intensity of radiation emitted or absorbed by an element is proportional to the atomic concentration of that element.

The emission intensity is detected by a detector which generates the electric signal. A monochromator is usually employed in this process. The signal is then amplified and displayed or recorded by the read out system. The unknown signals are compared with the signal of standard solution.

Approximately 10 grams of product oils were weighed and heated in a ceramic crucible on a hot plate at 75°C to vaporize most of the hydrocarbon. Then it was gently added with 20 milliliters of concentrated nitric acid and one milliliter of 30 % hydrogen peroxide. The mixture was allowed to boil on the hot plate to digest the sample until a homogeneous liquid mixture formed. Then they were diluted with deionized water to make the solution volume of 100 milliliters. These solutions were readily taken to analysis. Standard solutions used to prepare a calibration curve were metal-nitrate solutions, from Koch-Light Laboratories.