

CHAPTER 3

EXPERIMENTAL PROCEDURE AND RESULTS

3.1 DESIGN AND CONSTRUCTION OF THE REACTOR SET

A reactor set for carrying out experiments on hydrodesulfurization of light oils was constructed in the laboratory at the Department of Chemical Engineering, Chulalongkorn University. The maximum design pressure and temperature were 100 bars and 500 °C, respectively. The materials of construction were all stainless steel. Swagelok unions, joints and reducers, etc., were used because of their high reliability.

Fig. 3.1 shows a flow diagram of the high pressure through-flow reaction unit. Hydrodesulfurization of thiophene in toluene typically occurs via a reaction between sulfur compounds in the oil and hydrogen as below



Since hydrodesulfurization is carried out at medium high pressure, safety must come first. Before each experiment, N₂ is used to purge the reactor system, and again at the end of each experiment.

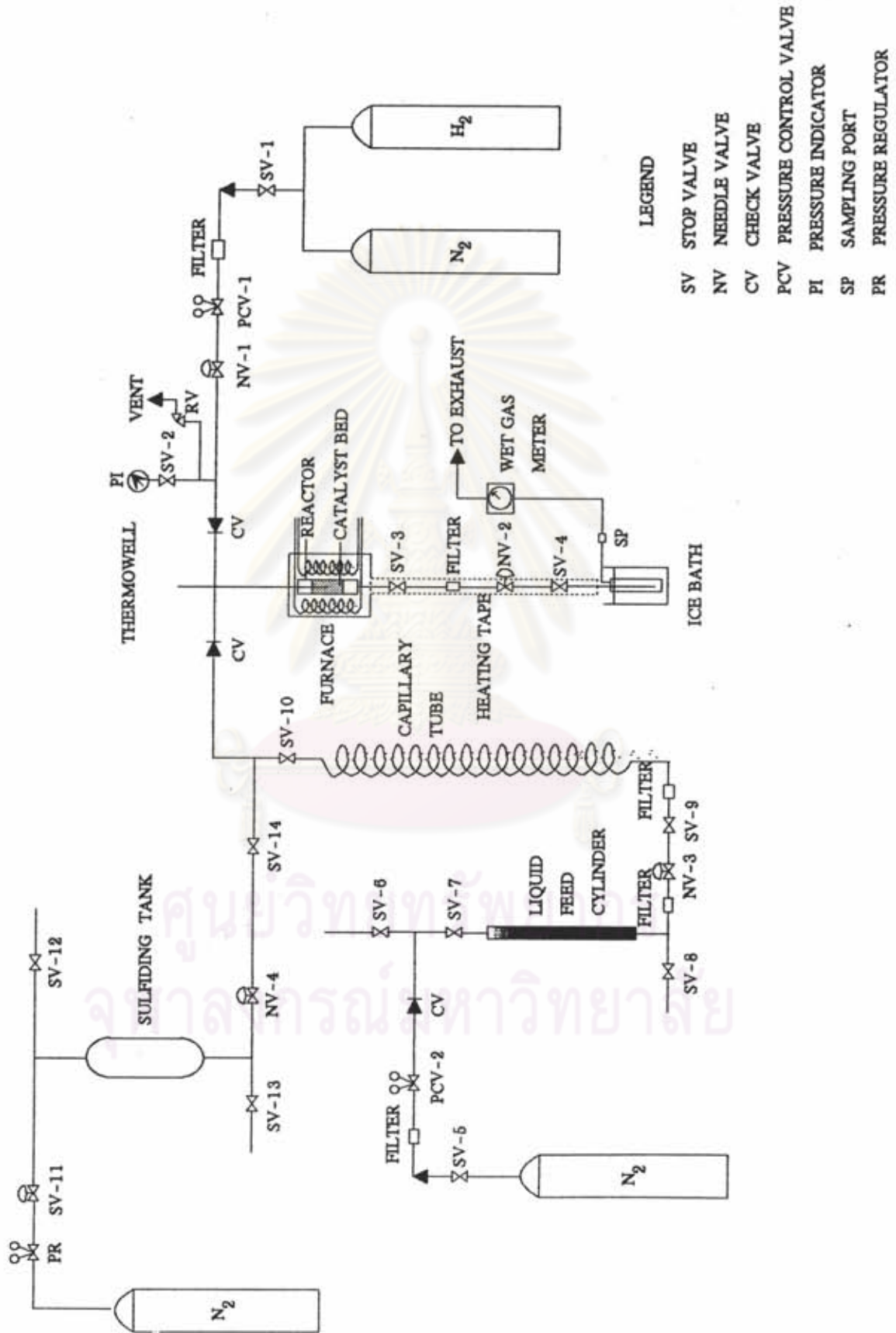


Figure 3.1 Flow diagram of the high-pressure through-flow reaction unit

During the experiment nitrogen pressure is used to feed the thiophene in toluene to the reactor column. The respective pressure control valves PCV1 and PCV2, pressure regulator PR are used to regulate and maintain the line pressures in this system at the desired values. Pressure indicators give the inlet and outlet pressures of each PCV and PR. Three needle valves NV3, NV4 and NV1 serve to adjust the flow rates of normal feed, feed for sulfiding and hydrogen or nitrogen, respectively. A pressure relief valve is provided to release any accidental build-up of pressure that might lead to an explosion. The reactor tube (1/2" O.D) is placed inside a uniformly heating furnace. Thermocouple sets are used to measure the temperatures of the catalyst bed in the reactor tube.

The outlet of the reactor has a needle valve (NV2) that is used to adjust the flow rate of the mixture and to reduce the outlet pressure to nearly atmospheric. Heating tape is used to prevent condensation of hydrocarbon vapor in the outlet line. An ice bath is used to condense most oil vapor. The condensate is separated and accumulated in a receiving pot. Dry gaseous sample is withdrawn at point SP. The wet-test meter measures the actual flow rate of the outlet gas.

The reactor set is supported on an angular steel framework (see Fig. 3.2). Because of the high inflammability of hydrogen, static pressure test for leakage is carried out step by step using N₂ at 5 bars, 10 bars, 20 bars, 30 bars, 40 bars, 50 bars, 60 bars and 70 bars, respectively, and using H₂ at 80 bars, 90 bars and 100 bars, respectively. At each test pressure, a soapy solution was squirted onto all areas susceptible to leakage, such as unions, joints, valve

handles, etc. Appropriate measures are taken to eliminate any detected leaks. During fabrication of the reactor set and in correcting the leaks, it is important not to turn any part tighter than necessary, since that might lead to irreparable damage.

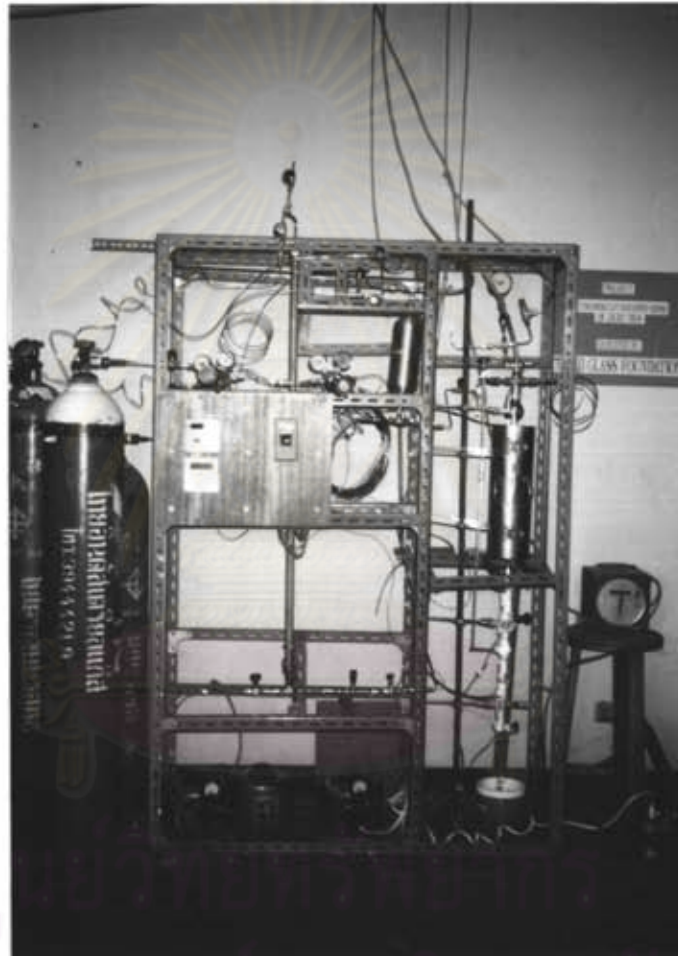


Figure 3.2 The reactor set for hydrodesulfurization

3.2 CONSTRUCTION OF THE ELECTRIC FURNACE AND MEASUREMENT OF ITS AXIAL TEMPERATURE DISTRIBUTION

The body of the heating furnace was made of refractory brick blocks. It was made by carving out 4 refractory brick blocks, inserting the electrical heating wires inside the grooves, and wrapping the four semicircular blocks in a thin metal sheet. To control the furnace temperature, the electric power supplied to the heating wires was adjusted using a slidac.

To ensure a uniform axial temperature distribution along the middle section of the constructed furnace, we measured the axial temperature distribution inside a 1/2" stainless tube which was placed in the furnace and, if necessary, adjusted the electric heating wires, so that axial temperature variations within $\pm 10^{\circ}\text{C}$ were achieved over the entire middle section of the furnace at 490°C .

Measurement of the axial temperature distribution was made by inserting a thermocouple probe into the stainless tube in the furnace after having set the desired temperature by adjusting the slidac. When the whole furnace had reached a steady state, the axial temperature distribution was measured with a sheathed CA (chromel-alumel) thermocouple. Based on the observed temperature distribution, specific portion of the electric wires were either stretched or compressed by trials and errors until the maximum axial temperature variation within the middle 12-cm region of the furnace was less than $\pm 10^{\circ}\text{C}$. Fig 3.4 shows the observed axial temperature distribution for the furnace under no-gas-flow conditions.

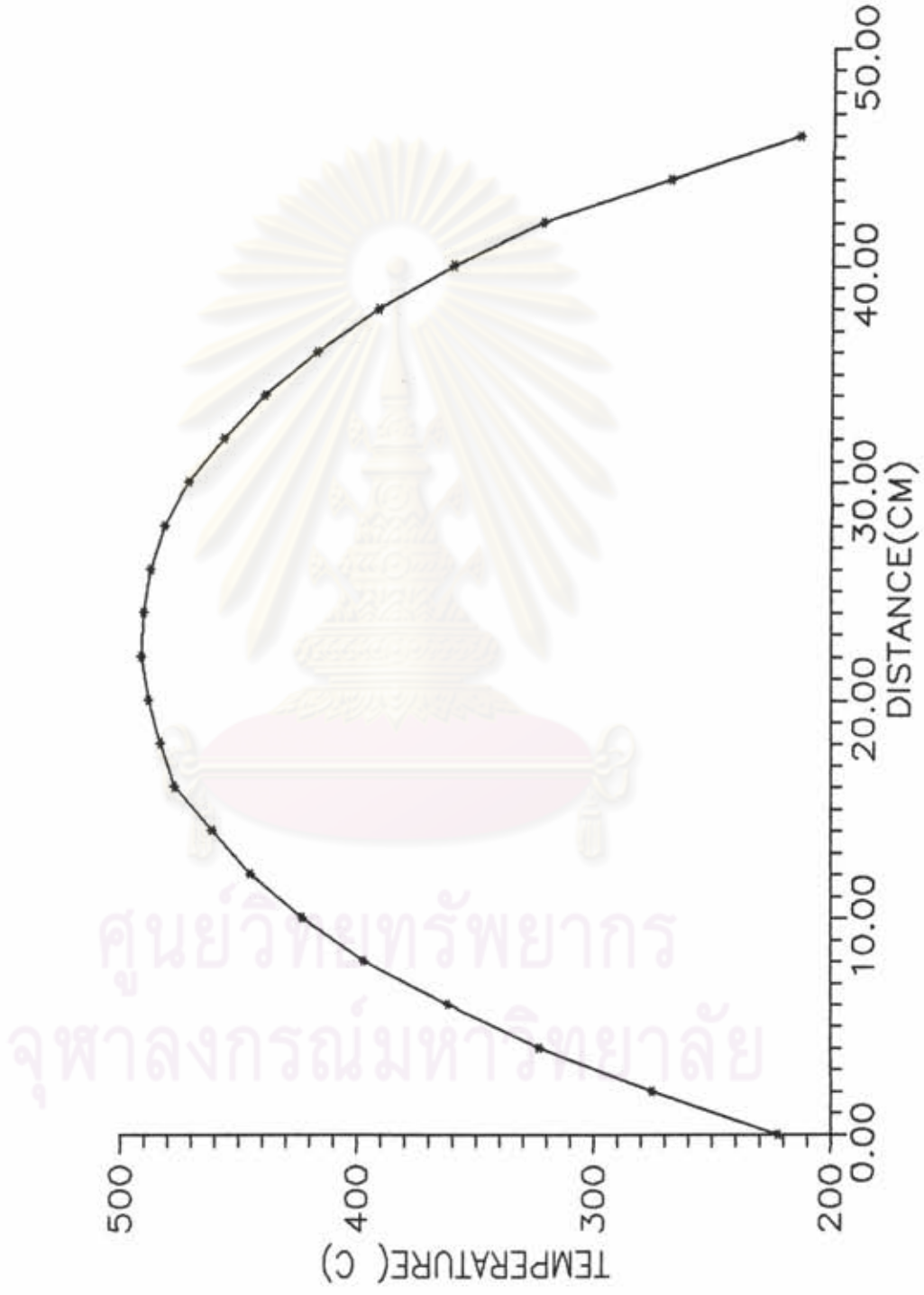


FIGURE 3.3 AXIAL TEMPERATURE PROFILE OF THE FURNACE



3.3 CATALYST PREPARATION

The steps of preparation were as follows:

1. An ammonium molybdate solution was prepared by dissolving 5.52 g of ammonium paramolybdate $[(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in distilled water, adding 1.5 ml of ammonia (28 % NH_3) and diluting with distilled water to 15 ml.

2. The above solution was added, while stirring, to an evaporating dish which contained 16.3 g of the alumina support (γ -type of 100 - 300 mesh size). The solution completely wetted the alumina support (incipient wetness 0.665 ml of solution per gram) and left no excess solution in the dish. The wet powder was dried at about 121°C for 24 hours.

3. A cobalt nitrate solution was prepared by dissolving 6.17 g of cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ in distilled water and diluting it to 10 ml. The solution was then added, while stirring, to an evaporating dish containing the dried alumina powder which had been impregnated with molybdenum. The solution completely wetted the molybdenum impregnated powder (incipient wetness 0.473 ml of solution per gram) and left no excess solution in the dish. The resulting wet powder was dried at about 121°C for 24 hours and then calcined in air in an electric muffle furnace at 482°C for about 10 hours. The final metal content of the catalyst was 5.14 % cobalt and 12.35% molybdenum.

To use in the experiments, the catalyst powder was compressed to obtain a pellet. The pellet was next cut up and screened to select fragment size between mesh #10 and #25. Then the classified fragments were packed into the middle section of the reactor for hydrodesulfurization experiment.

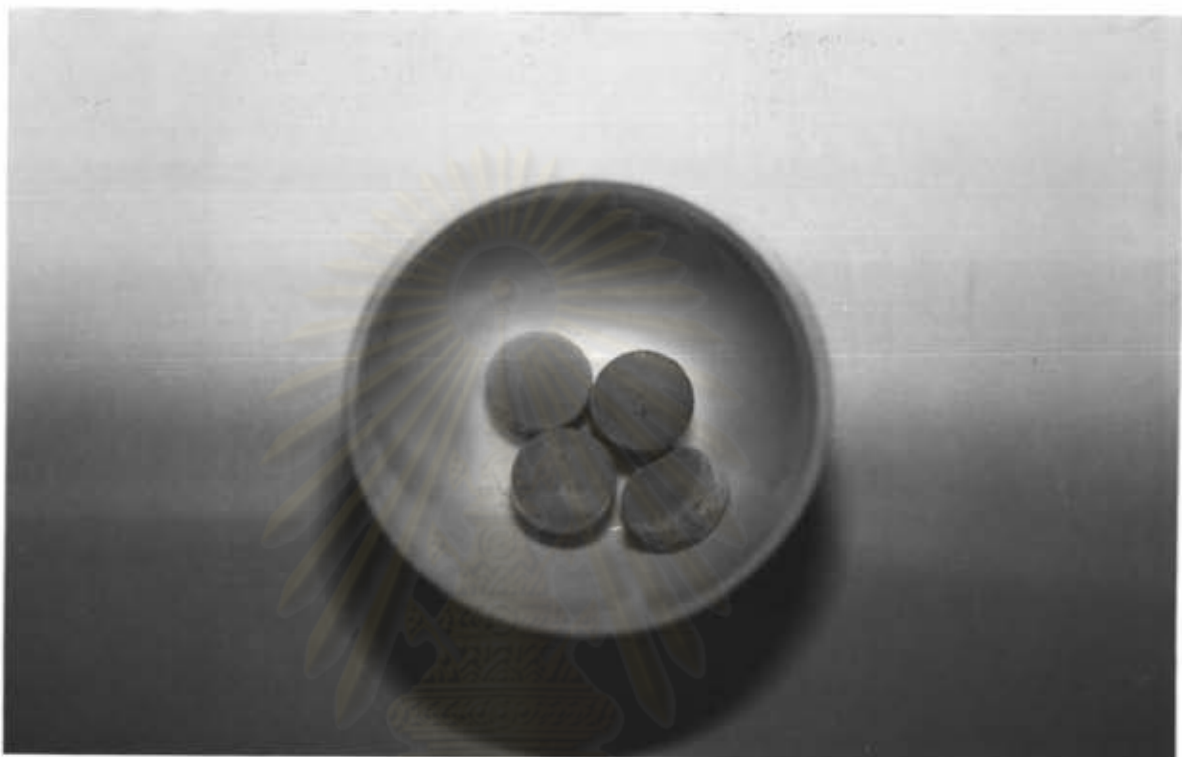


Figure 3.4 Catalyst pellet after compression.

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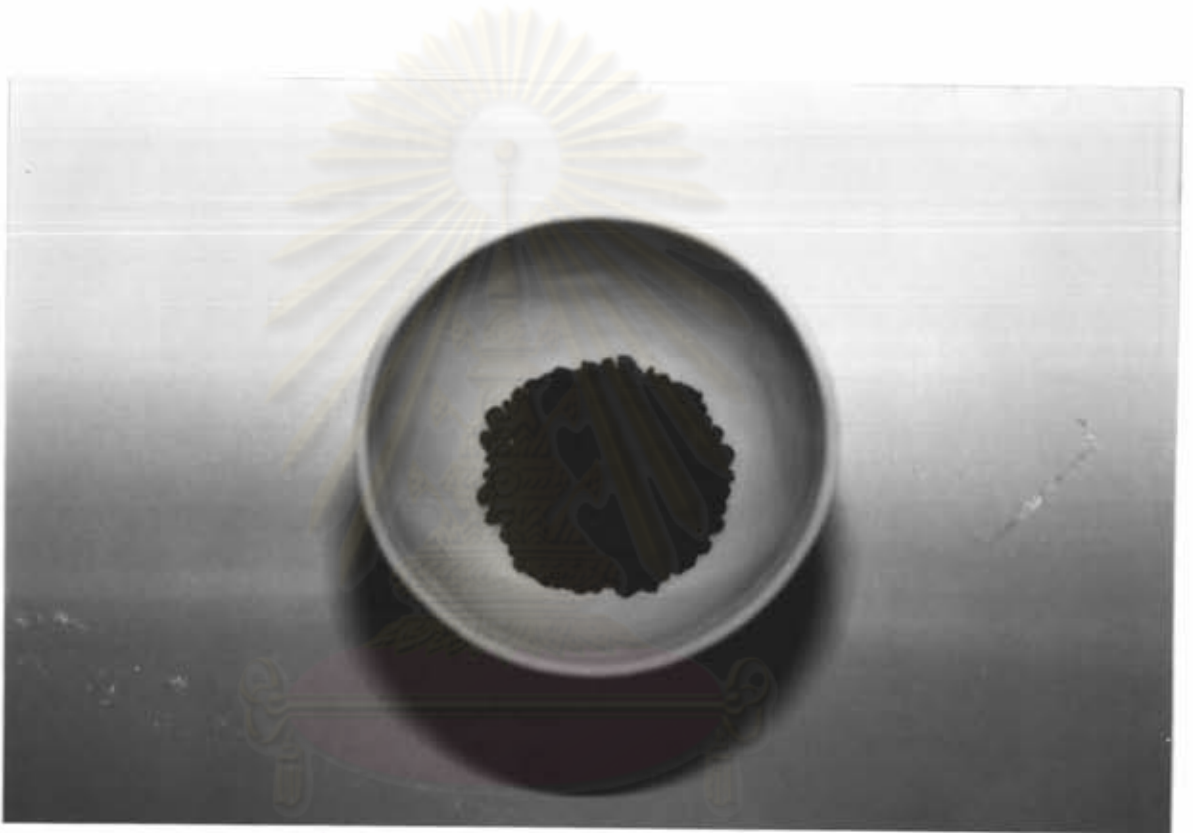


Figure 3.5 The reacted catalyst.

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3.4 REACTANT

Originally we had planned to study about hydrodesulfurization of light oil but because of limitation in the separation capability of the available FPD type GC apparatus and the fact that some light-oil's components have boiling points higher than that usable to the GC column we had to use a synthetic feed instead. Toluene had been chosen as the model feed because we learned that in the major component of motor gasoline was toluene and thiophene had been chosen as model reactant for the sulfur compounds because the typical order of reactivity of sulfur compounds showed thiophenic compounds as the least reactive in a petroleum fraction, and being the simplest and readily available compound in this class, thiophene itself, had frequently been chosen for study. The specifications of the synthetic feed were:

Thiophene C_4H_4S M.W. 84.14

purity > 98 % (GC); bp 82-84 °C; d 1.063

Toluene C_7H_8 M.W. 92.14

purity > 99.5% ; bp 111 °C; d 0.867

3.5 ANALYTICAL METHOD

Organic chemical compositions of liquid and gaseous samples were analyzed using Shimadzu GC-8AP_F gas chromatography equipped with a flame ionization detector (FID). The column was a 50 mL x 0.2 mm O.D. methyl silicone capillary column and its temperature was programmed from 33 °C (held for 11 min) to 100 °C at 1 °C/min. The injection/detector temperature was 120 °C.

Thiophene content of toluene before and after desulfurization was determined using Shimadzu Gc-8APF_p gas chromatography equipped with a flame photometric detector (FPD). The column was a 2.5 mL x 2.6 mm O.D. glass column packed with carbopack BHT 100 and set at to 110 °C. The injection/detector temperature was 110 °C.

3.6 EXPERIMENTAL PROCEDURE

In case of a fresh catalyst, it had to be sulfided before use. As mentioned in Chapter 2, the sulfiding technique that was used in this work was sulfiding with nonspiked feed because it was difficult to find H₂S, or to prepare spiked feed.

The procedure for presulfiding is as follows:

1. The two GC's (FID and FPD detectors) are started up, their conditions set and awaited until stability for analysis was obtained.
2. Prepare the wet test meter by pouring in clean water until the water level reaches the needle tip. Next connect both the inlet and outlet rubber tubes to the meter, and check for leak.

3. Open the shut-off valve of the N_2 cylinder, gradually open SV1, SV2, SV3 and SV4 to full open, turn the PCV1 knob to set the outlet pressure. Adjust NV1, NV2 and PCV1 until the desired flow rates and secondary pressure are obtained.

4. Switch on the heater of the furnace and the heating tape, set the reactor and heating tape temperature to 150 and 110 $^{\circ}C$, respectively, while drying the catalyst.

5. Open the shut-off valve of the other N_2 cylinder, open fully SV14, turn the N_2 pressure regulator to set the feed pressure at the reactor inlet. Adjust NV4 and SV11 to balance and get the desired feed rate.

6. Change over the gas in the gas feed line from N_2 to H_2 . Set the reactor temperature to increase at constant rate until 300 $^{\circ}C$ is reached.

7. Take a liquid sample and also take a gas sample through the sampling port. Analyze their hydrocarbon and thiophene compositions by the GC's.

8. After finishing presulfiding, shut off the hydrogen main valve and change over to nitrogen. Close SV11 and SV14, to stop the flow of feed, then open SV12 to release the N_2 gas pressure.

Start up procedure

1. Open the shut-off valve of the N_2 cylinder, open fully SV1, SV2, SV3 and SV4, turn the PCV1 knob to set the secondary pressure. Adjust NV1, NV2 and PCV1 until the desired flow rates and

pressure are obtained.

2. Switch on the heater of the furnace and the heating tape, set the reactor and tape temperature to 200 and 110 °C, respectively.

3. Open the shut-off valve of the other N₂ cylinder, open fully SV5, SV7 and SV10, turn PCV2 knob to pressurize the feed to be sent to the reactor. Adjust NV3, SV7, SV9 and PCV2 to balance and get the desired feed rate.

4. Wait until the flow rate of the feed is steady. Change over from N₂ to H₂. Raise the reactor temperature to the desired temperature. After reaching the desired temperature, start keeping the reaction time. At 0.5, 2.0, 4.0, 6.0, 8.0 and 10.0 hr take a liquid sample and measure the feed flow rate at the receiving pot. Also take a gas sample at the sampling port. Measure the flow rate of the outlet gas by the wet-test meter. Analyze for the hydrocarbon and thiophene compositions in the sample by the GC's.

5. After finishing the experiment, switch off the heater of the furnace and the heating tape. Shut off the hydrogen main valve and change over to nitrogen. Close SV5, SV7, SV9 to stop the flow of feed, open SV6 to release the gas pressure. When the reactor temperature drops to about 30 °C, close the main valve of nitrogen, as well as SV1, SV3, NV2 and SV4.

6. After obtaining the analysis results, turn off the GC's.