CHAPTER 4

EXPERIMENTAL EQUIPMENT AND PROCEDURE

4.1 Design and Construction of the High-Pressure Laboratory Unit

A high pressure tubular reactor system was constructed 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 valves and fittings were used throughout the reactor system.

The reaction section of the experimental apparatus consisted of a stainless steel tube of 23-inch length and 1/2 inch O.D., in which a thermowell was centrally installed to measure the reaction temperature with a sheathed thermocouple probe. The reactor tube was placed in an electrical furnace and the reaction temperature was controlled via the voltage supplied by two slidacs. The starting material consisted of n-heptane and hydrogen gas. The hydrogen gas was supplied to the reactor from a gas cylinder through a pressure control valve. The control valve was used to regulate the operating pressure of the feed H_2. n-Heptane feed was stored in a stainless steel cylinder and pressurised by nitrogen gas to the desired reaction pressure. The actual flowrate of the reaction gas was measured by a wet gas meter at the reactor outlet.

Figure 4-1 shows a flow diagram of the high-pressure reactor unit used in this investigation. Nitrogen gas was used to purge the

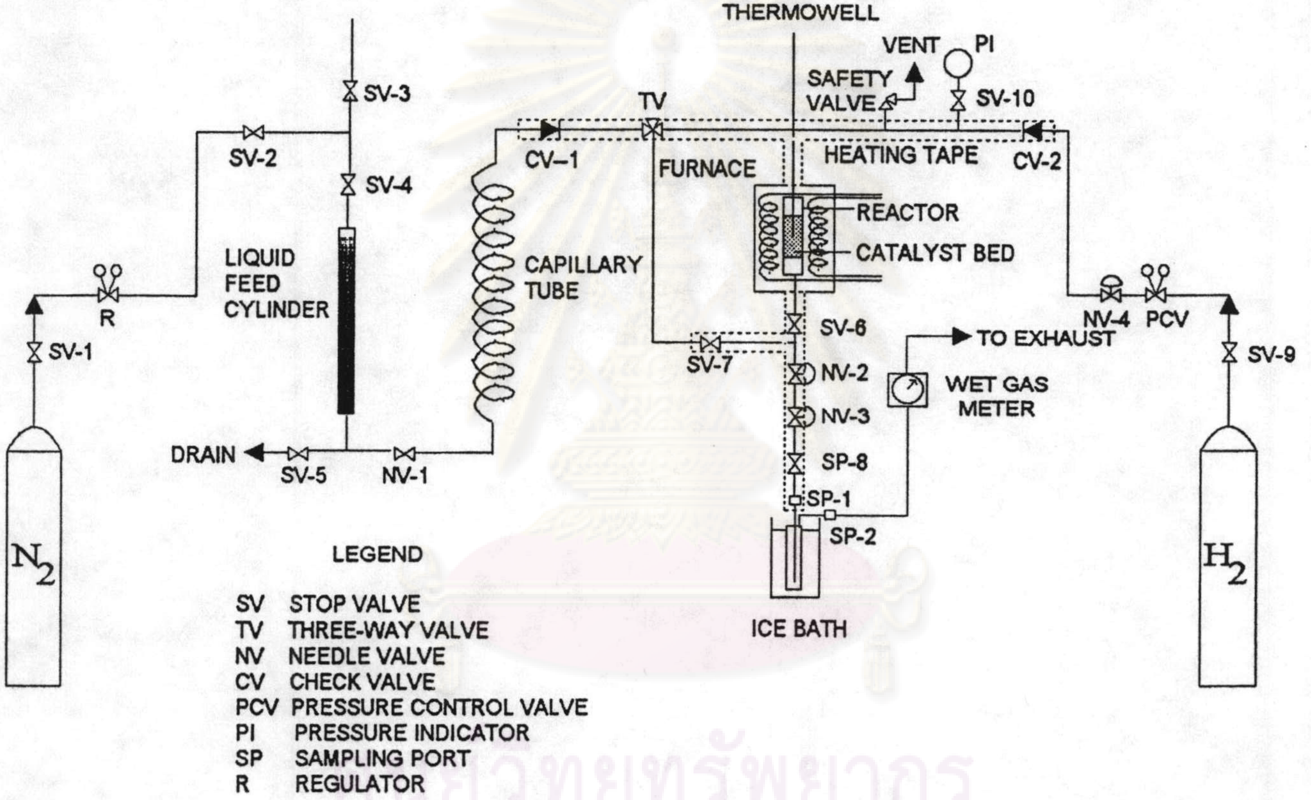

Figure 4-1 Flow Diagram of the High-Pressure Through-Flow Reaction Unit

system before and after each experiment. N_2 was also used to pressurize n-heptane to the operating pressure. Valves SV-1 and SV-9 were for the N_2 and H_2 cylinders, respectively. To regulate the pressure of the hydrogen gas, a pressure control valve was used. The PCV had two pressure indicators, one for the inlet and one for the outlet pressure. Needle valve NV-1 was used to adjust the inlet flow rate of n-heptane, whereas NV-4 was for hydrogen gas. In addition, a 40 m x 0.25 mm ϕ capillary tube was installed next to NV-1 in order to control the flow rate of n-heptane as low as possible. Needle valves NV-2 and NV-3, which were installed at the outlet of the reactor served to reduce the pressure and control the flow rate.

A safety valve was provided to release any accidental buildup of pressure that might result in an explosion. PI indicated the pressure in the reaction system. SP-1 and SP-2 were sampling ports. From the reactor outlet to the sampling port SP-1, the line was insulated and heated to prevent condensation of hydrocarbon vapours.

4.2 Leak Test of the Reactor Set

Because of the high inflammability of the hydrogen gas and the severe operating conditions, checking for leakage must be carried out at all points susceptible to leakage, such as unions, joints, valve handles, etc. In the first stage, that is from normal pressure to intermediate pressure (0-20 bars), nitrogen gas was used to test for leakage in the experimental apparatus. Next helium (He) gas was used for the high pressure test (20-100 bars). During the test, two methods were used to check for leak.

4.2.1 Soapy solution method

1. First open the outlet valve of the nitrogen (or helium) tank to supply gas into the experimental apparatus.

2. Increase and adjust the pressure of the gas in the experimental apparatus with the pressure control valve.

3. Squirt soapy solution onto all areas susceptible to leakage.

4. Wait and observe for the tell-tale appearance of gas bubbles. If bubbles are observed, then action, such as tightening of the joint, must be taken to stop the leak. Once no bubbles have been detected, return to step 2 and repeat the same procedure at a higher pressure (1, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 bars, respectively).

4.2.2 Static pressure test method

After the above soapy solution method has successfully been completed, a static pressure test is next carried out as follows:

1. Set the pressure in the experimental apparatus to the design pressure (100 bars), and shut off all the outlets.

2. Mark the position of the needle of the pressure gauge and after letting the unit stand for 24 hours, read the remaining pressure. If it is within 5% of the original value, the leak test is deemed to be successful. Otherwise, make careful inspection of all leak-prone areas and tighten them, if necessary. Then repeat the static pressure test as above.

4.3 Reconstruction of Electric Furnace and Measurement of Its Axial Temperature Distribution

The constructed furnace, which was designed to ensure isothermal operation of the reactor, was made of refractory bricks and heating wires. Four bricks were divided into two sides, each side consisting of two bricks longitudinally connected. Next a central hole was carved out of both sides such that the reactor tube might be placed snugly in it. Several small grooves were next carved out of the wall of the central hole to insert the electrical heating wires. Finally each side was wrapped in an aluminium or tin sheet, and the two sides were hinged together on one side edge, so that the furnace could be opened easily when catalyst was to be charged or discharged.

The reaction temperature was controlled by two sliding voltage devices to vary the voltage of the heating wires. Measurement of the axial temperature distribution was made by inserting a thermocouple probe into a stainless tube placed inside the furnace. When the whole furnace had reached a steady state, the axial temperature distribution was measured with the sheathed CA (Chromel-Alumel)thermocouple. Based on the observed temperature distribution, specific portions of the electrical heating wires were stretched or compressed accordingly by trials and errors until the maximum axial temperature variation within the middle 10 cm region of the furnace was less than ± 5 ^{o}C at 500 ^{o}C. The observed axial temperature distributions with no gas flow inside stainless tube are shown in Figure 4-2.

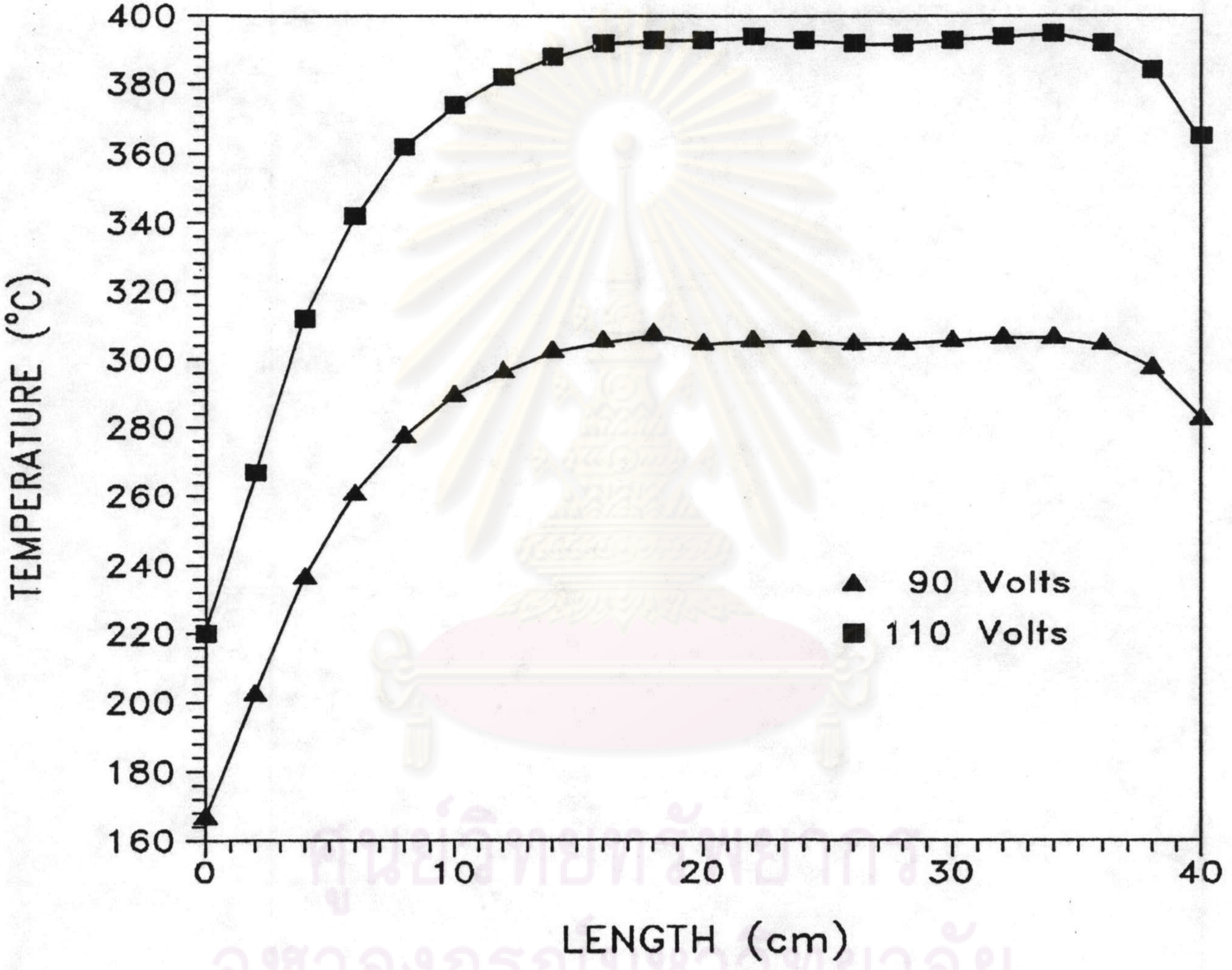

Figure 4-2 The Observed Axial Temperature Distribution

4.4 Preparation of Catalysts

Zeolitic catalysts used for this research were kindly supplied by TOSOH Corp.,Japan. They were transformed to the protonic form by ion exchange. First an ammonium solution was used to change the sodium form to the ammonium form, and then the catalyst sample was dried and calcined to drive off the ammonia gas, rendering the catalyst the active protonic form.

HM Catalyst

The preparation procedure of the HM catalyst was as follows:

1. The Na-mordenite powder was continuously stirred in NH_4NO_3 solution at 90°C for 2 hours.

2. The mordenite catalyst in step 1 was filtered and washed with distilled water.

3. The mordenite in step 2 went through step 1 and 2 a second time, and then was filtered and washed three more times with distilled water.

4. The resulting NH_4-mordenite catalyst was dried at 120°C in an oven for 1 day.

5. The NH_4-mordenite catalyst was calcined in open air at 450°C for 8 hours in order to drive off ammonia gas, thus resulting in H-Mordenite (HM) catalyst.

Chemical reactions concerning the modification of the Na-mordenite catalyst are :

i) $\text{Na-mordenite} + NH_4^+(sol^n) \xrightarrow[90^\circ C]{stir} NH_4\text{-mordenite}$

ii) $NH_4\text{-mordenite} \xrightarrow[Calcine]{450^\circ C} \text{H-mordenite} + NH_3(g)$

HY Catalyst

The preparation procedure of the HY zeolitic catalyst consisted of the same five steps of the HM preparation. Chemical reactions concerning the modification of the Na-Y catalyst are :

i) $\text{Na-Y} + NH_4^+ (sol^n) \xrightarrow[90^\circ C]{stir} NH_4\text{-Y}$

ii) $NH_4\text{-Y} \xrightarrow[Calcine]{450^\circ C} HY + NH_3(g)$

0.5 wt% Pt/HM Catalyst

Pt/HM catalyst was prepared from H_2PtCl_6 and HM zeolite by the impregnation technique. Drying and calcination were carried out as above.

0.5 wt% Pt/HY Catalyst

HY was impregnated with chloroplatinic acid solution. Drying and calcination were carried out as above.

0.5 wt% Pt/USY Catalyst

Ultrastable Y zeolite (USY) was impregnated with H_2PtCl_6 solution. Drying and calcination were carried out as above.

0.5 wt% Pd/HM Catalyst

Pd/HM catalyst was prepared from $PdCl_2$ and HM zeolite by the impregnation technique. Drying and calcination were carried out as above.

0.5 wt% Pd/HY Catalyst

HY was impregnated with palladium (II) chloride solution. Drying and calcination were carried out as above.

0.5 wt% Pd/USY Catalyst

USY was impregnated with palladium (II) chloride solution. Drying and calcination were carried out as above.

Table 4-1 Composition of Zeolites Studied (TOSOH Corp.)

ZEOLITE TYPE COMPOSITION	Na-Y HSZ-320 NAA	Na-Mordenite TSZ-620 NAA	USY HSZ-330 HUA
SiO_2 (wt %) dry basis	66.5	84.3	78.0
Al_2O_3 (wt %) dry basis	20.7	9.4	21.7
Na_2O (wt %) dry basis	12.8	5.5	0.10
SiO_2/Al_2O_3 (mole ratio)	5.5	15.3	6.1
Na_2O/Al_2O_3 (mole ratio)	1.02	-	0.01

4.5 Catalyst Loading

The following steps constitute the catalyst loading procedure:

i) 1.5 ml of the calcined catalyst sieved 20 to 30 mesh was weighed and its weight was recorded.

ii) The catalyst was placed on a fine stainless steel screen set in the middle region of the reactor tube. In addition, two glass-wool pads were placed in the reactor tube, one at the top and the other at the bottom of the catalyst bed.

iii) The reactor tube was set in its place. Then leak test was carried out stepwise up to a pressure at least 20% higher than the planned maximum operating pressure, first using nitrogen and then helium at higher pressures.

iv) Before carrying out the hydroisomerization runs, the catalyst was first reduced in-situ to the active metallic form by passing a flow of hydrogen over the catalyst at 500^{o}C.

4.6 Reactants

The reactants used were n-heptane (J.T.Baker Inc., 99.9 mol%) and hydrogen gas (99.999% purity) without any dilutant. The reactants were fed at the desired pressure to the tubular through-flow reactor without any purification.

4.7 Analytical Method

The chemical composition of the liquid and gaseous products was determined by gas chromatography. A Shimadzu FID gas chromatograph (model 8 APrF), equipped with a 50 m x 0.2 mm ϕ methyl silicone capillary column and a sample splitter, was used to analyze C_3 and higher hydrocarbons. To detect the hydrogen and C_1-C_2 hydrocarbons, a Shimadzu TCD gas chromatograph (model 8 AT) equipped with a MS-5A column and a Porapak Q column was used.

4.8 Experimental Procedure

Before starting each experimental run, it is necessary to switch on the two GC's and wait until they are ready for analysis (usually about 1 hour). Then start the experiment by following the procedure below.

a. Open the valve of the N_2 gas cylinder and purge the reactor system in Figure 4-1 with N_2 for 15 minutes at nearly atmospheric pressure.

b. Shut off the N_2 gas and then open the valve of the H_2 gas cylinder and turn the PCV knob to let hydrogen flow through the catalyst bed at the desired pressure.

c. Adjust the flow rate of H_2 to obtain the desired value with the aid of NV-2 and NV-3. Use a wet-test flow meter to measure the flow rate.

d. Next set the reactor temperature to $150^{o}C$ by applying voltage to electric furnace.

e. Open the valve of N_2 to pressurize n-heptane to the operating pressure and adjust the flow rate of n-heptane to obtain the desired value with the aid of NV-1.

f. Wait until steady state condition has been reached. After that, the temperature of the reactor and sampling port were recorded, in addition to theflow rate of gaseous product and liquid product and the pressure of the system.

g. Analyze the gaseous product and liquid product with the Shimadzu Gas Chromatographs.

h. Raise the reactor temperature to another desired reaction temperature, namely, 240°, 260°, 280°, 300° and 320°C, respectively.

i. Take the gaseous product and liquid product to analyze at each reaction temperature whenever a new steady atate condition had been achieved.

j. After the experimental run had been finished, turn off the slidacs and gradually cool down the reactor while decreasing the pressure in the reactor.

k. When the reactor temperature drops to 70°C, shut off the the H_2 gas valve and substitute the H_2 gas with N_2 gas.

l. Purge the system with N_2 gas until there is no hydrogen gas left in the system. Use the gas chromatograph for confirmation.

m. Shut down the gas chromatographs according to the manuals.