

CHAPTER 3

EXPERIMENTAL EQUIPMENT AND PROCEDURE

3.1 CONSTRUCTION OF EQUIPMENT

The equipment used in this study was constructed at the Department of Chemical Engineering, Chulalongkorn University, and designed to operate up to 100 atm in pressure, 400 °C in temperature for the reactor section, and 100 atm, 200 °C for the liquid feed section. Swagelok valves and fittings were used to connect to the various sizes of stainless steel seamless tubes.

3.1.1 Flow Diagram

A complete flow diagram of the experimental equipment is shown in Figure 3-1. It consisted of three main sections, namely feed section, reactor section and product recovery section. Some devices required in the experiment are not shown in the diagram, such as sets of temperature controllers for controlling the temperature of liquid feed section and reactor section. In addition, not shown are the heating wires for preventing the condensation of the liquid feed and the products in the recovery region, three sets of temperature probes, and their measuring circuits.

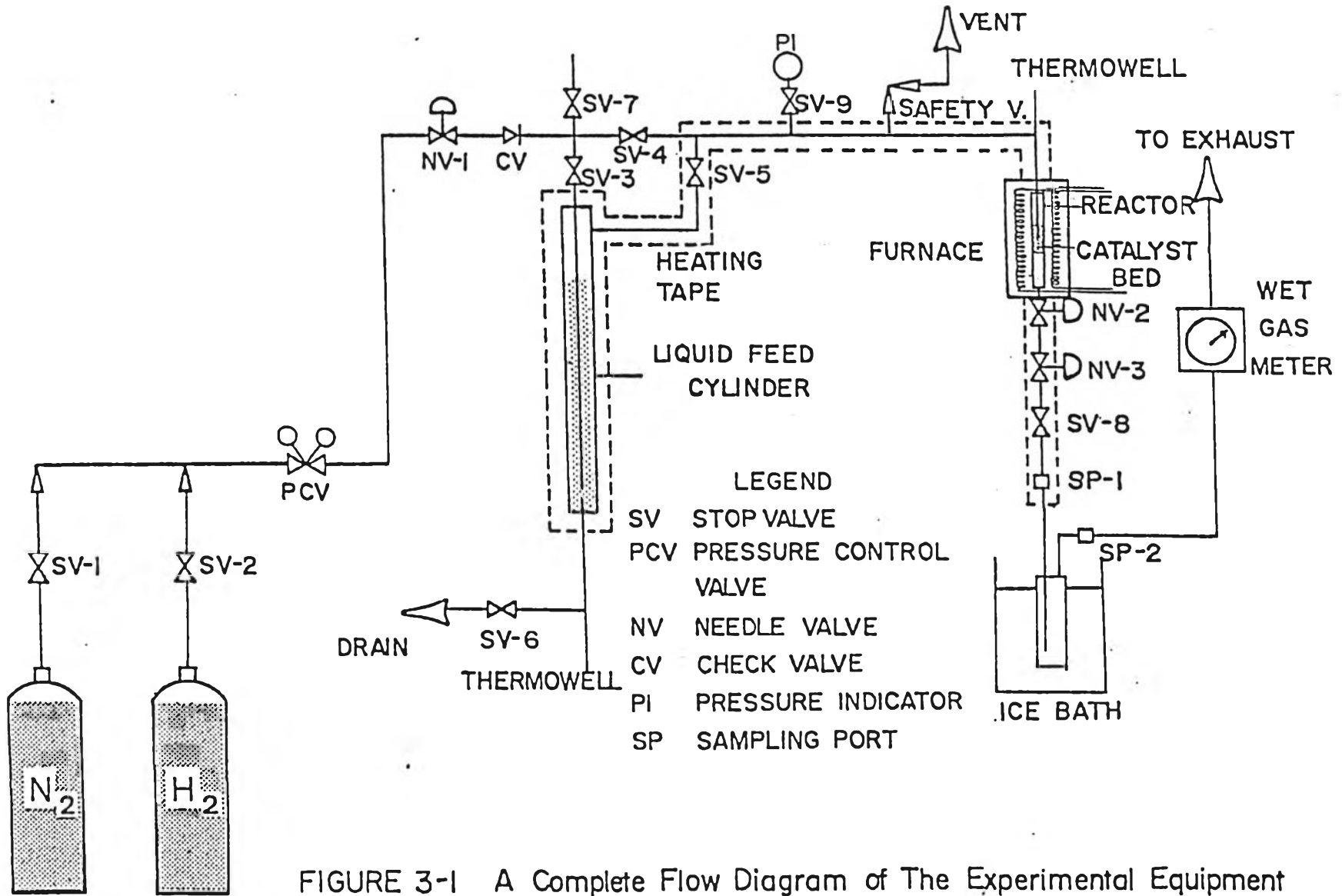


FIGURE 3-1 A Complete Flow Diagram of The Experimental Equipment

3.1.2 Feed Section

The n-hexane feed was prepared by vaporizing the pure liquid contained in the reactant cylinder, made of 1-inch O.D. seamless stainless steel tube. The heat required to vaporize the liquid n-hexane was supplied from the surrounding heating wires. In addition, heating tapes were used to warm up the tubing leading to the reactor in order to prevent condensation of the gaseous feed on its way to the reactor section. The temperature of the liquid was measured via a thermowell placed inside the cylinder.

Hydrogen from a gas cylinder was sent through a filter before adjusting its outlet pressure with a pressure control valve. Next the hydrogen gas was sent through the liquid n-hexane tank which made the liquid temperature nearly uniform, and the resulting gas mixture, containing hydrogen and n-hexane vapor, went out through a union tee connected at the top of the liquid tank to the reactor section.

3.1.3 Reactor Section

The fixed-bed down-flow reactor used in the experiments was made of seamless stainless steel tube, $\frac{1}{2}$ inch in diameter and 22 inches in length. The reactor was designed to withstand a maximum pressure of 100 atm at a maximum temperature of 400 °C. It was also designed for ease

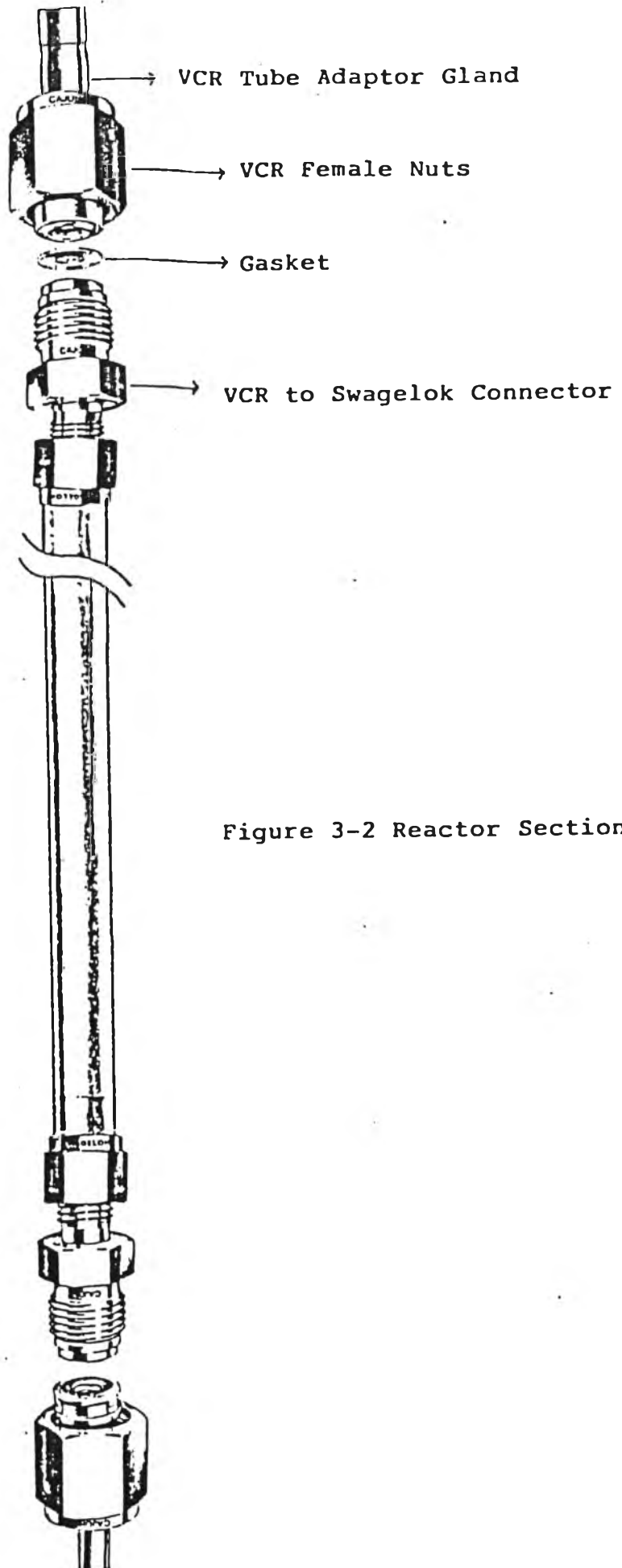


Figure 3-2 Reactor Section

of connection and disconnection required when catalyst was charged and discharged. Therefore, special Swagelok fittings had to be used, namely, VCR tube adaptor glands, VCR to Swagelok connectors, VCR female nuts and gaskets, connected to both ends of the reactor tube, as shown in Figure 3-2. The reaction temperatures within the catalyst bed were measured using three sets of CA type thermocouples placed inside a thermowell at the center of the reactor tube. The thermocouples were connected to a temperature indicator to read out and record the operating temperatures.

3.1.4 Product Recovery Section

Samples of the product gas were taken for analysis through sampling port 1 or sampling port 2. The former was closer to the reactor tube than the latter, and the line between the reactor and the former was warmed to prevent condensation of any vapors in the product gas. Heating tape was used for this purpose, as in the case of reactant feed section. After the first sampling port, the product gas went through an ice bath to condense out the vapor fractions before going to the second port. After the dry gas sample was taken at the second sampling port, the remaining gas was vented through a wet gas meter to the atmosphere.

3.2 ELECTRIC FURNACE

3.2.1 Construction of Electric Furnace

The constructed furnace, which was designed to ensure isothermal operation of the reactor, was made of refractory bricks and heating wires, as shown in figure 3-3.

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 four bricks to insert the electrical heating wires. Finally each side was wrapped in an aluminium-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 and discharged.

3.2.2 Test of Axial Temperature Distribution

The reaction temperature was controlled by two slide voltage devices to vary the voltage of the heating wires. Measurement of the axial temperature distribution was made by placing a stainless tube inside the furnace, and the axial temperature inside the tube was measured using a sheathed CA (Chromel-Alumel) thermocouple set. To ensure isothermal operation, Three sets of axial temperature

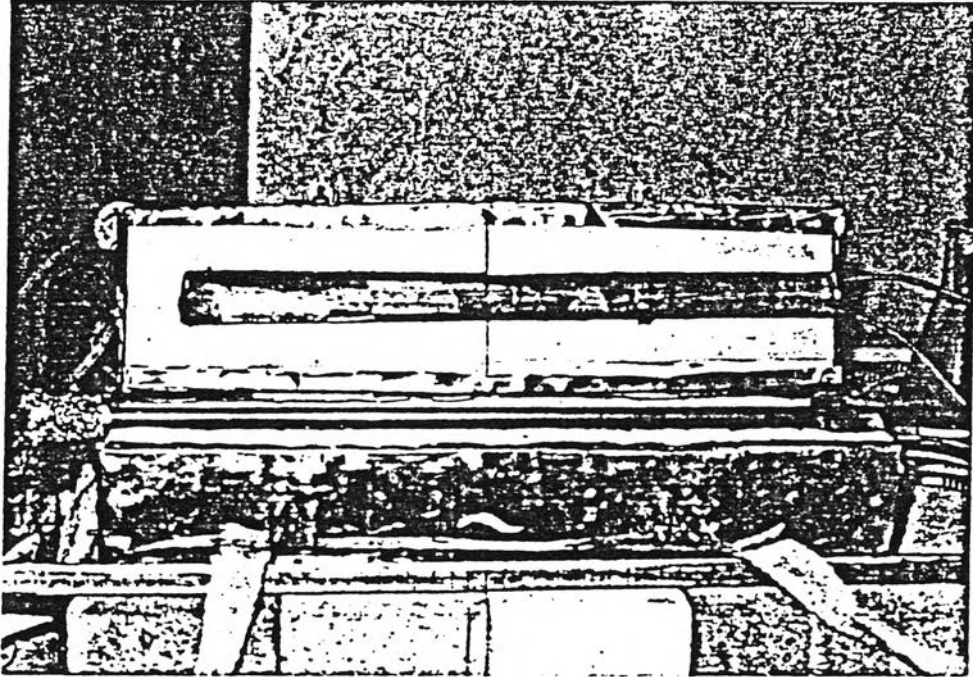


Figure 3-3 The Constructed Electric Furnace.

distribution, each with less than ± 3 °C variation in the middle region of the furnace, were achieved for a length not less than 10 centimeters. The observed axial temperature distributions with no gas flow inside stainless tube are shown in Figure 3-4.

3.3 ANALYTICAL INSTRUMENT

Two dual-column Shimadzu Gas Chromatographs were used to analyze the components of the reactant feed and product gas. Model 8 APrF was used to analyze carbon containing gaseous components, and model 8AT was used to analyze the hydrogen gas component. A VZ-7 column, 5 meter long, was used to separate the hydrocarbon components, and the column temperature was set at 40 °C. The other column used in model 8AT to analyze hydrogen component was MS-5A, 5 meter long, set at 125 °C. The proportionality constants relation peak areas to mole fractions and additional details are given in Appendix B.

3.4 PREPARATION OF CATALYSTS USED.

The catalyst powder was modified to the active form, pelleted, crushed and then screened to the desired size. The catalysts thus obtained was calcined immediately before use in the experiments.

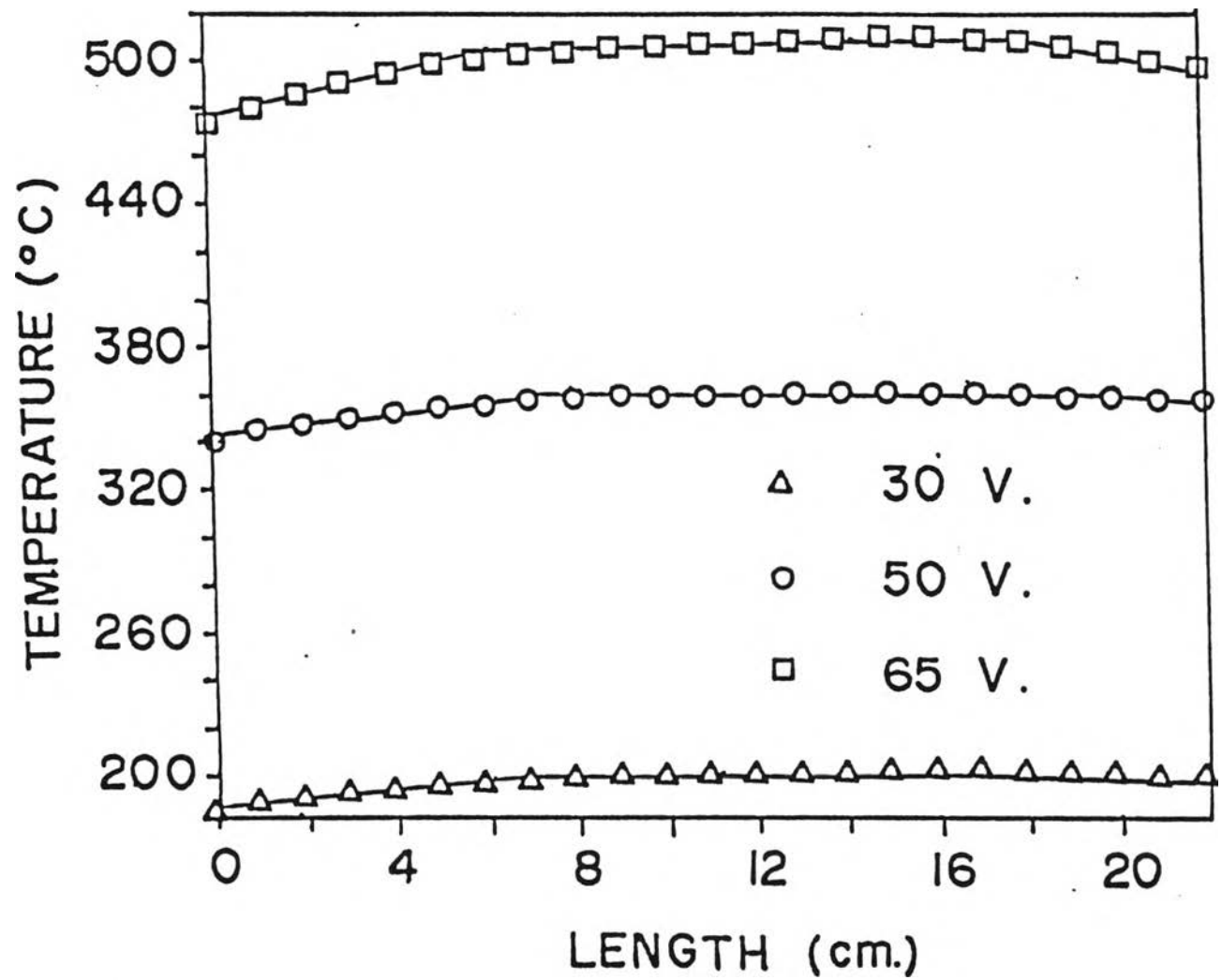


Figure 3-4 The Observed Axial Temperature Distribution

The purpose of the above modification was to change the the Na-form to the protonic form by ion exchange. First an ammonium solution is used to change the sodium form to the ammonium form, and then calcined to drive off the ammonia gas, rendering the catalyst the active protonic form.

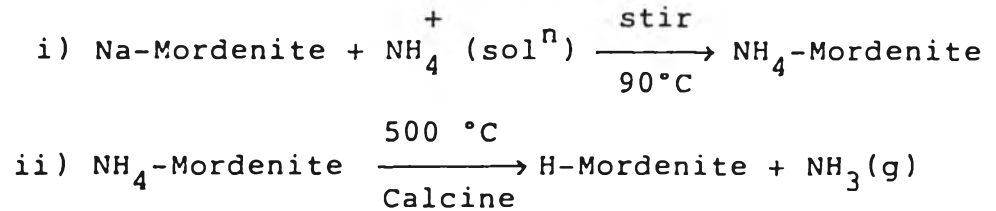
3.4.1 Na-Mordenite Preparation

The preparation procedure of Na-mordenite zeolitic catalyst was as follows :

1. Three grams of the Na-mordenite powder was continuously stirred in 45 ml. of 10% 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. Pelleted and then crushed into various sizes, the catalyst fragments were screened using 20-and 24-mesh sieves.
6. The screened NH_4 -mordenite catalyst was calcined in open air at 500 °C for 15 hours in order to

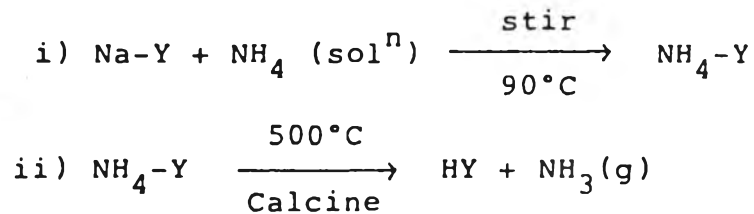
drive off ammonia gas, thus resulting in H-mordenite catalyst, the acidic active form for hydrocracking reaction.

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



3.4.2 Na-Y Preparation

The preparation procedure of Na-Y zeolitic catalyst was the same as the six steps of the Na-mordenite preparation. Chemical reactions concerning the Na-Y preparation are :



3.5 EXPERIMENTAL PROCEDURE

3.5.1 Leak Test of Experimental Equipment

After fabrication has been finished, to make sure that the apparatus was safe to operate at the maximum design pressure, a pressurized gas test was made using nitrogen. First nitrogen at 5 atg. was introduced into the

apparatus. Then a soapy solution was used to find out any possible leakage points by squirting the solution onto all areas susceptible to leakage, such as the connections of unions and tubes, the connections of valves and tubings, etc. Subsequently, pressures of the compressed nitrogen was raised step by step from 10, 20, 30, 40, 50, 70, 90 until 100 atg while carrying out the same leak test procedure as at 5 atg. Finally, the above test was repeated using hydrogen gas instead of nitrogen.

The leak testing of the experimental apparatus need to be carried out whenever the spent catalyst had to be replaced with a fresh catalyst.

3.5.2 Catalyst Loading

The following steps constitute the catalyst loading procedure :

i) Two cc. of the calcined catalyst 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 at a pressure at least 20% higher

than the maximum operating pressure, first using nitrogen and then hydrogen at higher pressures.

3.5.3 Experimental Procedure

The experimental procedure is as follows :

i) While S.V.2, S.V.6 and S.V.7 were shut off, nitrogen was first used to purge the system before the start of each experimental run.

ii) Temperature of the reactor was raised to 100°C and kept constant by adjusting the slide voltage devices.

iii) After 30 minutes of nitrogen purging S.V.1, S.V.3 and S.V.5 were shut off, and S.V.2 was opened to let hydrogen flow through the catalyst bed at the desired pressure for 30 minutes, Simultaneously the liquid feed was heated up to the desired temperature and kept constant at that temperature.

iv) S.V.4 was shut off while S.V.3 and S.V.5 were opened.

v) The flow rate of the feed gas mixture was set by adjusting the two needle valves at the outlet of the reactor tube, and the flow rate was measured using the wet gas meter and a stop watch.

vi) Wait until steady state condition has been reached. After that, the temperatures of the liquid feed, reactor and sampling port were recorded, in addition to the

total flow rate of gas mixture and the pressure of the system.

vii) A sample of the product gas mixture was taken each at sampling port 1 and 2, and then analyzed with the Shimadzu Gas Chromatographs.

viii) The reactor temperature was raised to another desired reaction temperature, namely 260, 280, 300, 320 and 340 °C, respectively.

ix) Gas sample was taken to analyze the products at each reaction temperature whenever a new steady state condition had been achieved.

x) After the experimental run had been finished, the temperature of both reactor and reactant feed were lowered as nitrogen was sent through the apparatus instead of hydrogen.

3.5.4 Data Recording

When each sample of the outlet gas mixture was taken for analysis, the following information was recorded :

- i) Catalyst bed temperature
- ii) System pressure (at the reactor inlet)
- iii) Liquid feed temperature
- iv) Temperature of the sampling port
- v) Flow rate of the gas mixture

The experimental conditions investigated in the hydrocracking of n-hexane are summarized as follows :

Catalyst type	:	Na-mordenite and Na-Y
Pressure	:	30, 50 and 95 atg. for Na-mordenite 50 and 70 atg. for Na-Y
Temperature	:	260, 280, 300, 320 and 340°C
Space Velocity	:	2000, 4000 and 8000 hr ⁻¹