

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

Equipment

A gas chromatograph (GC) equipped with an FID detector and a ULBON[®] PLC capillary column (Shinwa Chemical Industries Ltd.)

A pump, model M-45 solvent delivery system (Milipore[®] Water Associates)

A fraction collector, model 2110 (BIORAD[®])

Fittings

3-way ball valves 2500 psig, 1/8" OD Tube ends (Hylok)

Male connector, OD 1/16" x 1/8" MNPT (Hylok)

Reducing union, OD 1/16" x 1/8" (Hylok)

Union, OD 1/16" (Hylok)

Teflon ferrule 1/4" (Swagelok)

Backpressure regulator 500 psi (Upchurch Scientific)

Chemical

1,5-dimethylnaphthalene (96 % purity Aldrich)

Zeolites

20-40 mesh sieved Beta zeolite in the hydrogen form (24 SiO₂/Al₂O₃, 25% alumina binder: UOP LLC)

The Na exchanged faujasite zeolites (Chemical compositions shown in Table 3.1: UOP LLC)

Table 3.1 Chemical compositions of Na-exchanged faujasite zeolites.

| Adsorbent | Chemical Composition |
|-----------|---------------------------------------------------------|
| 2.0NaX | $\text{Na}_{96}(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$ |
| 2.5NaX | $\text{Na}_{84}(\text{AlO}_2)_{84}(\text{SiO}_2)_{108}$ |
| 5.0NaY | $\text{Na}_{53}(\text{AlO}_2)_{53}(\text{SiO}_2)_{139}$ |
| 12.0NaY | $\text{Na}_{25}(\text{AlO}_2)_{25}(\text{SiO}_2)_{167}$ |

Solvents

Benzene (99 % purity, Fisher Scientific)

Ethylbenzene (99.8% purity, Aldrich)

1,4-diethylbenzene treated silica gel (pDEB) (98 % purity, Acros)

1,2-xylene (o-xylene) treated silica gel (99 % purity, Sigma Aldrich)

1,3-xylene (m-xylene) treated silica gel (99 % purity, Sigma Aldrich)

1,4-xylene (p-xylene) treated silica gel (99 % purity, Aldrich)

N-nonane treated silica gel (99 % purity, Aldrich)

3.2 Methodology

3.2.1 Catalytic Isomerization Experiments

3.2.1.1 Batch Isomerization

Catalytic isomerization of 1,5-DMN along the 2,6-triad route was batch-wisely conducted using an autoclave reactor. The reactant was prepared by dissolving a solid feedstock, 10 wt% 1,5-DMN, into one of the employed solvents. All solvents were treated by silica gel before being used, except benzene which was used as received. Then, the 5 wt% of 20-40 mesh sieved H-beta zeolite was poured into the autoclave. After that, the autoclave was heated to the desired temperatures and held for 2 hours with shaking every 45 minutes. The effects of each solvent on the catalytic isomerization were studied at 180°, 190°, and 220°C. The products after the isomerization were quantitatively and qualitatively analyzed by a gas chromatograph (GC) equipped with an FID detector and the ULBON® PLC capillary column which can separate all isomers of DMN from each other.

3.2.1.2 Continuous Isomerization

A suitable solvent was selected to study the isomerization in a continuous flow fixed-bed system. The experimental apparatus was set up as shown in Figure 3.1. For all experiments, 3 ml of H-beta zeolite was packed in a 3/8-in ID stainless steel reactor to perform the reaction at the desired temperature. Quartz wool was used to block the catalyst at both ends of the column. In order to prevent solvent vaporization at elevated temperatures, all experiments were carried out at 500 psi, which is sufficiently higher than the vapor pressure of the solvents. The solvent was sent to the reactor at the liquid hourly space velocity (LHSV) of 30 h⁻¹ until the system reached the desired pressure. Then, the flow was switched to feed the solution of 10 wt% 1,5-DMN. The fraction collector was started to collect the effluent every 2 minutes. The effluent was sampled for analyzing by the gas chromatograph (GC).

The effect from the temperature was initially investigated by varying the temperature in the range of 180-240°C and plotting the temperature profile versus the product composition. Equilibrium constants for each isomerization step in the reaction were calculated for the solvent systems based on the ideal solution assumption following Equation 3.1:

$$K_{i-j} = \frac{\alpha_j}{\alpha_i}, \quad (3.1)$$

where α is the mole fraction of the DMNs distributed in the 2,6-triad at equilibrium. The subscripts i and j represent the reactant and product species in each reaction step.

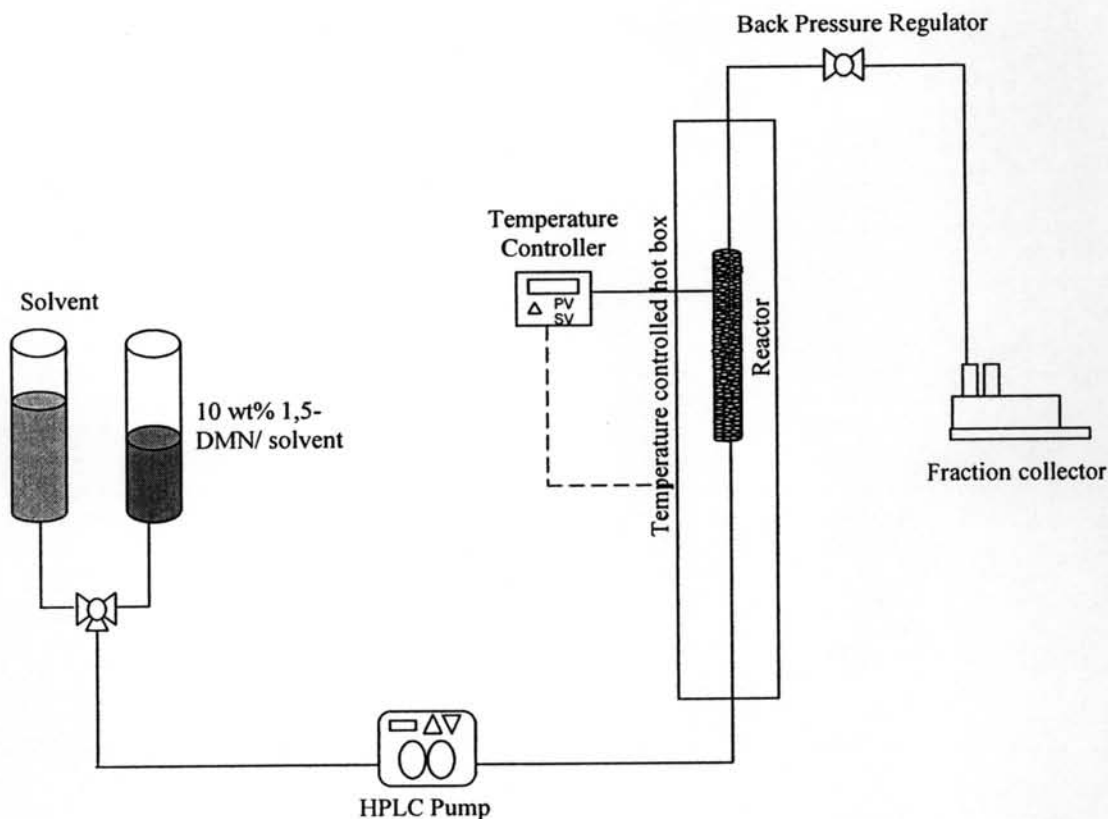


Figure 3.1 Experimental setup for the continuous isomerization experiment.

3.2.2 Dynamic Adsorption Experiments

The pulse test was employed to study the effects of using a solvent as a desorbent. Firstly, the equilibrium solid mixture of 2,6-triad DMNs consisting of 8 wt% 1,5-DMN, 43 wt% 1,6-DMN, and 49 wt% 2,6-DMN was prepared following the conditions presented elsewhere (Kraikul *et al.*, 2006a). Then, 10 wt% of the DMNs equilibrium mixture was prepared in a desired desorbent to be used as a feed. Five weight percent of n-nonane was also added into the feed as a tracer. Na-faujasite zeolites were calcined at 350°C for 1 hour before being used as adsorbents.

Experimental pulse testing was conducted using the experimental apparatus shown in Figure 3.2. The adsorbent was packed into a 70 ml stainless steel adsorber before being subsequently filled with the selected desorbent with a fixed flow rate of 1.2 mL/min, equivalent to 1 h⁻¹ LHSV. After the system reached a desired temperature and pressure of 180°C and 500 psi, 5 ml of a feed mixture was

injected into the adsorber. The effluent was collected using a fraction collector for quantitative analysis using GC equipped with an FID detector and the ULBON[®] PLC capillary column. An elution profile was then plotted between the composition and the retention volume of the effluent. By comparing the retention volume of the tracer to those of the DMNs, the net retention volumes (NRV) were obtained. The relative adsorption selectivity of the species was then calculated using the ratio between the NRVs of the two interesting species.

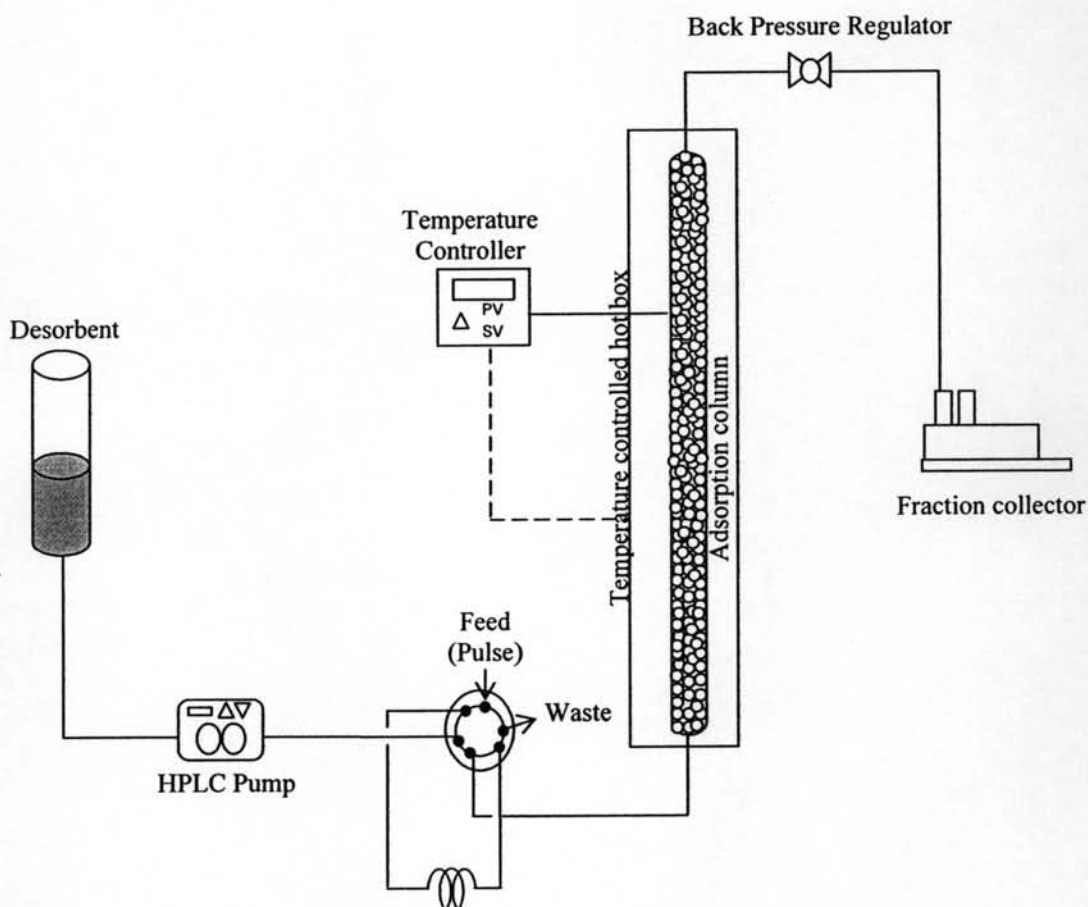


Figure 3.2 Experimental setup of the pulse test experiment.