

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Acidic catalysts used in this study were H-beta (24 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 25% alumina binder, UOP LLC, USA), H-mordenite (20 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 30% alumina binder, UOP LLC, USA), and H-ZSM5 (20 Si/Al 20% alumina binder, UOP LLC, USA) in the size range of 20-40 mesh. The alkaline and alkaline earth ion-exchanged faujasite zeolites used as adsorbents were obtained from UOP LLC (USA) as listed with their chemical compositions in Table 3.1. Prior to the experiments, the catalysts and adsorbents were dried at 250°C for at least 3 hours, particularly for the adsorbents to keep their losses on ignition (LOI) below 7. Chemicals used were 1,5-dimethylnaphthalene (96% purity, Aldrich, USA), toluene (99.9%, Fisher Scientific, USA) and n-heptane (99%, Aldrich, USA), which were utilized as received.

**Table 3.1** Chemical composition of the alkaline and alkaline earth exchanged faujasite zeolites used as adsorbents

Adsorbent	Chemical Composition	Adsorbent	Chemical Composition
LiX	Li <sub>20</sub> Na <sub>64</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	LiY	Li <sub>22</sub> Na <sub>31</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
NaX	Na <sub>84</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	NaY	Na <sub>53</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
KX	K <sub>82</sub> Na <sub>2</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	KY	K <sub>51</sub> Na <sub>2</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
RbX	Rb <sub>71</sub> Na <sub>13</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	RbY	Rb <sub>47</sub> Na <sub>6</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
CsX	Cs <sub>73</sub> Na <sub>11</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	CsY	Cs <sub>49</sub> Na <sub>4</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
MgX	Mg <sub>30</sub> Na <sub>24</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	MgY	Mg <sub>20</sub> Na <sub>13</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
CaX	Ca <sub>40</sub> Na <sub>4</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	CaY	Ca <sub>23</sub> Na <sub>7</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
SrX	Sr <sub>41</sub> Na <sub>2</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	SrY	Sr <sub>24</sub> Na <sub>5</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>
BaX	Ba <sub>41</sub> Na <sub>2</sub> (AlO <sub>2</sub> ) <sub>84</sub> (SiO <sub>2</sub> ) <sub>108</sub>	BaY	Ba <sub>24</sub> Na <sub>5</sub> (AlO <sub>2</sub> ) <sub>53</sub> (SiO <sub>2</sub> ) <sub>139</sub>

### 3.2 Study on Catalytic Melt Isomerization (Without Solvent)

All isomerization experiments of 1,5-dimethylnaphthalene (1,5-DMN) were carried out in a Pyrex<sup>®</sup> reactor operated in a batch mode. The reaction temperature was controlled by an E5CN Omron temperature controller equipped with a K-type thermocouple submerging into the solution. A magnetic stirrer was also employed to distribute the solid catalysts throughout the liquid reactant.

A sampled product of around 0.3 g from each isomerization reaction was dissolved in 2 mL of toluene to be a representative sample of the testing condition. The solution was manually injected into a HP gas chromatograph (GC) equipped with Carbowax<sup>®</sup> 20m (Supelco 2-4085) capillary column that can separate the isomers of DMN from each other and a flame ionization detector (FID) for quantitative analysis. The column temperature was initially set at 120°C before being gradually increased to 200°C with a 2°C/min ramping rate after the sample injection. Subsequently, the column temperature was continuously increased to 250°C with a rate of 15°C/min and held at that temperature for 20 min to complete the analysis.

For all experiments, around 4.6 g of 1,5-DMN (96% purity, Aldrich, USA) as a reactant was physically mixed with a solid catalyst for the isomerization reaction at a specific temperature and atmospheric pressure. After the desired reaction time was achieved, the reaction was suddenly stopped by cooling the solution temperature to room temperature and a portion of solid product was sampled for further analysis.

Amount of H-beta was varied from 1 – 5 wt% to investigate effects of catalyst amount on isomerization product distribution. Three catalysts, H-beta, H-mordenite, and H-ZSM5, were used to study their performance to isomerize 1,5- to 2,6-DMN. The reaction temperature and reaction time were also fixed at 265°C and one hour, respectively. A catalyst and its amount that provided the highest activity were then used to study effects of reaction temperature. The temperatures of 175, 200, 225, 235, 250, 255, and 265 °C were used with a constant reaction time of one hour.

The best catalyst amount and type from the above experiments were then used for the reaction equilibrium limitation study. Results were also analyzed for

equilibrium constants of the reactions involving in isomerization of 1,5-DMN in the 2,6-triad. The reaction temperatures were varied from 235, 240, 250, 255, 260, and 265°C and the experiments were performed until all species concentrations were constant. Subsequently, thermodynamic analysis of the system was performed.

### **3.3 Study on Catalytic Isomerization in Toluene Media**

Catalytic isomerization of DMN was conducted in a continuous flow fixed bed system in this study. For all experiments, 5 mL of 20-40 mesh sieved commercial H-beta zeolite was employed as a catalyst and packed in a 3/8-in ID stainless steel reactor. A solid feedstock, 1,5-DMN, was prior dissolved in toluene to the desired concentrations before being fed to the reactor with the desired flow rate. In order to prevent the solvent vaporization at elevated temperatures, all experiments were carried out at 500 psi, which is sufficiently higher than the vapor pressure of toluene. The products after the isomerization were quantitatively and qualitatively analyzed by a gas chromatograph (GC) equipped with an FID detector and the ULBON<sup>®</sup> PLC capillary column (Shinwa Chemical Industries Ltd., Japan) that can separate all isomers of DMN from each other.

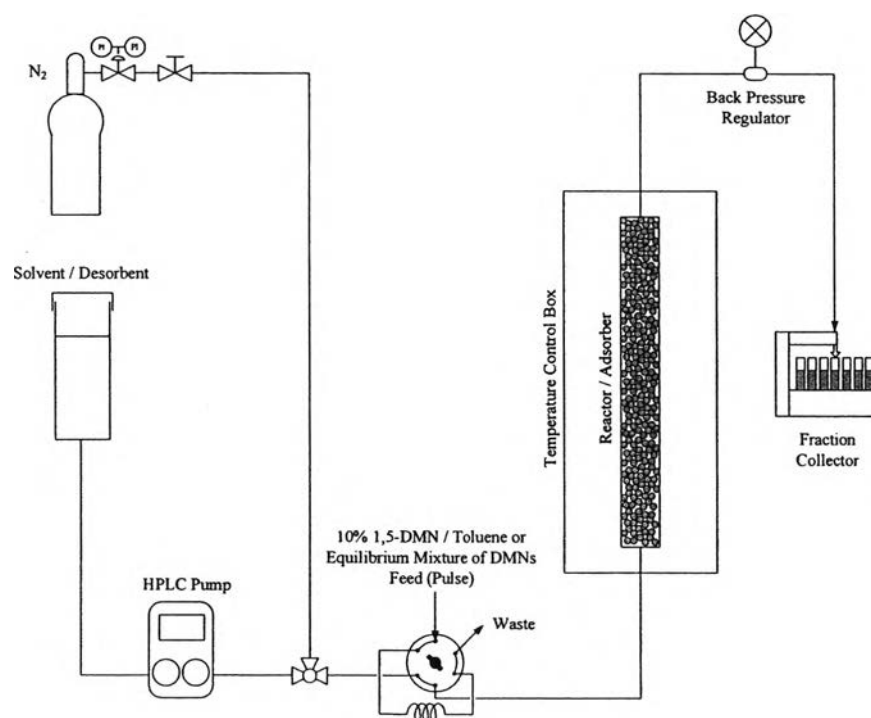
The effect of feed flow rate was initially investigated by varying the liquid hourly space velocity (LHSV) from 10 to 110 h<sup>-1</sup> while fixing the feed concentration and reaction temperature at 10 wt% and 180°C, respectively. A flow rate, which has no mass transfer effect, was then used for the study of reaction temperature effect within a range of 150°C to 260°C. After that, the effect of feed concentration was investigated by varying the 1,5-DMN concentration from 1 to 30 wt%, which is close to its maximum solubility in toluene.

### **3.4 Study on the Adsorption of DMN over Ion-exchanged Faujasite Zeolites**

The equilibrium mixture of DMNs was synthesized from catalytic isomerization of 1,5-DMN in toluene over H-beta catalyst following the best condition suggested from the previous study. The total concentration of DMN was

fixed at 10 wt%, which composes 8%, 43% and 49% of 1,5-, 1,6- and 2,6-DMN, respectively. For all experiments, n-heptane was added into the equilibrium solution as a tracer.

Experimental pulse test was conducted over ion-exchanged faujasite zeolites using the experimental apparatus as shown in Figure 3.1. The adsorbent was packed into a 70 mL stainless steel adsorber before subsequently filled with toluene, which was a desorbent in this study. The flow rate of the desorbent was fixed at 1.2 mL/min, equivalent to  $1 \text{ h}^{-1}$  LHSV. After the system reached the desired temperature and a pressure of 500 psi, 5 mL of a feed mixture was then injected into the adsorber and the effluent was collected using a fraction collector for quantitative analysis by means of a gas chromatograph (GC) equipped with a Stabiwax-DB<sup>®</sup> capillary column and a FID detector. Relative adsorption selectivity of the species was then calculated using the ratio between the net retention volume (NRV) of the two interested species.



**Figure 3.1** Experimental set up for catalytic isomerization, adsorption and reactive adsorption studies using the pulse test technique.

For studying the effect of temperature, the pulse test experiments were carried out at 40, 100, 160, 180 and 200°C for NaY. Effects of exchanged cation on the DMNs adsorbability on the employed faujasite zeolites were also investigated at a fixed temperature of 180°C. The adsorbents providing a high potential for being used in 2,6-DMN separation were also identified from the experimental pulse test results. After that, the high concentration study was performed using the breakthrough technique. In this study, the feed was not diluted by the solvent as in the case of the pulse test; thus, the effect of feed concentration would be observed. The experiment was performed following the same procedure of the pulse test, except the equilibrium mixture was continuously pumped to the adsorber. After a 100 mL of the feed had been pumped into the adsorber, the desorbent was then fed to desorb the DMNs from the column. Adsorption capacity and selectivity of the selected adsorbents were calculated. Comparison between those from the low concentration study (pulse test) and high concentration study (breakthrough test) was then made.

### **3.5 Study on the Combinations of Catalytic Isomerization and Adsorption**

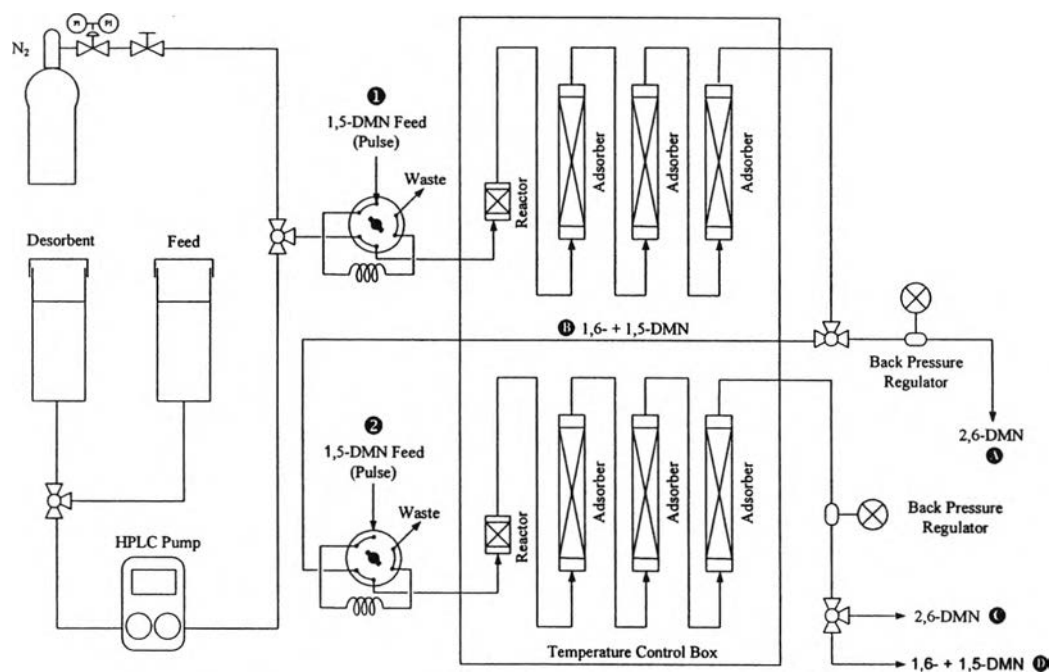
Before studying the production of 2,6-DMN using the combined systems of isomerization and adsorption, the two processes were individually studied using the same pulse test apparatus illustrated in Figure 3.1. For the isomerization study, acidic beta zeolite as a catalyst was packed into a 3 mL stainless steel reactor before subsequently filled with toluene, which was a reaction media. The feed flow rate and reaction temperature were varied to study their effect on the isomerization. After the flow rate and the temperature of the system reached their desired set point with a pressure of 500 psi, 5 mL of 10 wt% of 1,5-DMN in toluene as a feedstock was then injected into the reactor, and the effluent was collected using a fraction collector for quantitative analysis by means of a gas chromatograph (GC) equipped with a Stabiwax-DB<sup>®</sup> capillary column and a FID detector.

For the adsorption study, the experiment was conducted following the procedure of the isomerization study, except the feedstock was the synthesized

equilibrium mixture of DMN consisting of 8%, 43% and 49% of 1,5-, 1,6- and 2,6-DMN, respectively, of a total concentration of 10 wt%, with n-heptane as a tracer. In addition, the potential adsorbent suggested from the previous study was packed into the column with varied quantities from 15 to 75 mL of a 15 mL interval instead of the catalyst.

Then, the study on 2,6-DMN production by subsequently conducting the adsorption after the isomerization was performed using the experimental setup as shown in Figure 3.2. Three mL of the catalyst was used with the appropriate liquid hour space velocity (LHSV), reaction temperature and adsorbent amount as suggested by the previous experimental results. Firstly, 10 mL of 10 wt% of 1,5-DMN in toluene as a feedstock was injected into the reactor and adsorber to observe the DMNs profiles generated from the isomerization and subsequent separation over the catalyst and adsorbent, respectively. Afterwards, an experiment with a removal of high purity 2,6-DMN from the isomerized products was conducted. In this experiment, the 1,5- and 1,6-DMN rich stream after the high purity 2,6-DMN withdrawal was re-injected into the reactor and adsorber, simulating its utilization as a recycle stream to be further isomerized. In addition, studying by re-injecting 10 mL of the feed together with the 1,5- and 1,6-DMN rich stream, and by continuously feeding 30 mL of the feedstock instead of pulsing the feed were conducted. The ratios between the isomerized product to the reactant in each isomerization step from each experiment were also calculated to evaluate the performance of such the technique reached the maximum yield of 2,6-DMN at equilibrium.

Possibility of using the reactive adsorption technique for producing high purity 2,6-DMN was subsequently investigated by conducting the experiment following the same procedure using the same apparatus as that of the isomerization study (Figure 3.1), except 45 mL of a physically mixed H-beta/NaY with the fixed ratio similar to the previous study was packed into the column. The reaction temperature, feed flow rate, and catalyst to adsorbent ratio were also varied to investigate their effect on the production and equilibrium of the isomerization.



**Figure 3.2** Experimental set up for study the production of 2,6-DMN by connecting the adsorbers subsequently to the reactor.