

CHAPTER V

UNEXPECTED ROLES OF TOLUENE IN THE CATALYTIC ISOMERIZATION OF 1,5- TO 2,6-DIMETHYLNAPHTHALENE*

5.1 Abstract

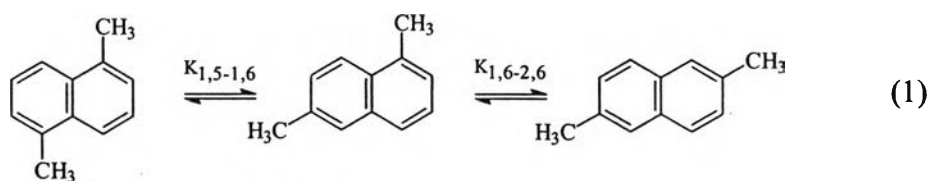
Catalytic isomerization of 1,5- to 2,6-dimethylnaphthalene (DMN) over H-beta zeolite was carried out in a continuous flow fixed bed system by using toluene as a solvent in this study. Feed flow rates, reaction temperatures and feed concentrations were varied to investigate their effect on the isomerization in the presence of the solvent. Interestingly, it was found that the presence of toluene leads to the modification of the reaction thermodynamics, resulting in the ease of the isomerization to be occurred at significant lower temperatures, besides its roles to facilitate the reaction for the flow system by dissolving the solid reactant (1,5-DMN) and enhance the system mass transfer. As a result, the maximum yield of 2,6-DMN as in the high temperature equilibrium of the solvent-free system could possibly be approached at even low temperatures when the system is not limited by mass transfer of the DMN species and the reaction kinetics.

5.2 Introduction

2,6-Dimethylnaphthalene (DMN) is a precursor for the high-performance engineering plastics and liquid crystal polymers production, e.g. polyethylene naphthalate (PEN) [1-3]. The cost of 2,6-DMN is relatively high and mostly controls the cost of the polymer due to its high complexity in multiple steps synthesis and purification [3]. Presently, only a large scale process of BP Amoco has been successfully commercialized. The process employs four reactions-in-series, starting from alkylation, cyclization, dehydrogenation and complete with isomerization. By processing the feed stock (toluene and butadiene) through the first three reactions,

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1,5-DMN is claimed to produce with the high 90s conversion and selectivity [3], and is subsequently isomerized to the desired 2,6-isomer in the last isomerization unit. Consequently, 1,5-DMN is batch-wisely isomerized to 1,6- and 2,6-DMN following the below reaction, which is called the 2,6-triad route. As the reaction is thermodynamically controlled, only 48% yield of 2,6-DMN can be achieved when the reaction approaches its equilibrium under controlled conditions [1, 3-5].



Until now, the isomerization has been usually accomplished in a solvent-free system over acidic zeolites with little attention on the use of a solvent [5-10]. For the solvent-free isomerization, the best catalyst is H-beta zeolite [4-5, 7]. Our previous work investigated the speciation of DMN as a function of temperature over the zeolite [4] and suggested that the reaction needs to be carried out at least 250°C to reach its equilibrium with the maximum yield of 2,6-DMN [4-6]. However, at that high temperature, side products of around 0.5 – 2.5 wt% are usually generated [4-5, 7], which also consequently increase the difficulty in 2,6-DMN purification besides the lost of the desired chemical.

In this contribution, an attempt to carry out the catalytic isomerization over H-beta zeolite in a continuous flow fixed bed system was conducted using toluene as a solvent to dissolve the solid reactant. Effects of toluene on the isomerization were investigated and comparatively discussed with those of solvent-free system [4]. Equilibrium constants of the solvent system were also calculated to preliminarily illustrate the unexpected roles of toluene on the isomerization.

5.3 Experimental

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 (24 SiO₂/Al₂O₃, 25% alumina binder, UOP LLC, USA)

was employed as a catalyst and packed in a 3/8-in ID stainless steel reactor. A solid feedstock, 1,5-DMN (96%, Aldrich, USA), was prior dissolved in toluene (99.9%, Fisher Scientific, USA) 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[®] 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⁻¹ 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.

Equilibrium constants for each isomerization step in reaction (1) were calculated for the solvent systems based on the ideal solution assumption following equation (2). Both magnitude and variation with concentration and temperature of the constants were compared and with those of the solvent-free system [4].

$$K_{i-j} = \frac{\alpha_j}{\alpha_i}, \quad (2)$$

where α is the mole fraction of DMNs distributed in the 2,6-triad at equilibrium. The subscripts i and j represent the reactant and product species in each reaction step. The thermodynamic properties of each isomerization step were then calculated following our previous procedure described elsewhere using the Gibbs-Helmholtz equation [4].

5.4 Results and Discussion

5.4.1 Effect of Feed Flow Rate

The effect of the feed flow rate was initially investigated for a fixed feed concentration and reaction temperature of 10 wt% and 180°C, respectively. Fig. 5.1 shows the relative concentration profiles of the DMN species from different feed flow rates. As expected, the increase in the feed flow rate suppresses the isomerization of 1,5-DMN to 2,6-DMN, and not more than 30 h⁻¹ LHSV should be used to avoid this effect for the testing condition. At the flow rate higher than 30 h⁻¹ LHSV, 1,6-DMN and 2,6-DMN are still only products without any intermediates from the catalytic isomerization of 1,5-DMN in the toluene system. This result suggests that the presence of toluene as a solvent for the isomerization does not change the desired isomerization route. Interestingly, the profile of 1,6-DMN is barely affected by the change in the contact time, while those of the other two DMNs are. This result indicates that there might be some incidents occurred with the molecule in the toluene system than the others.

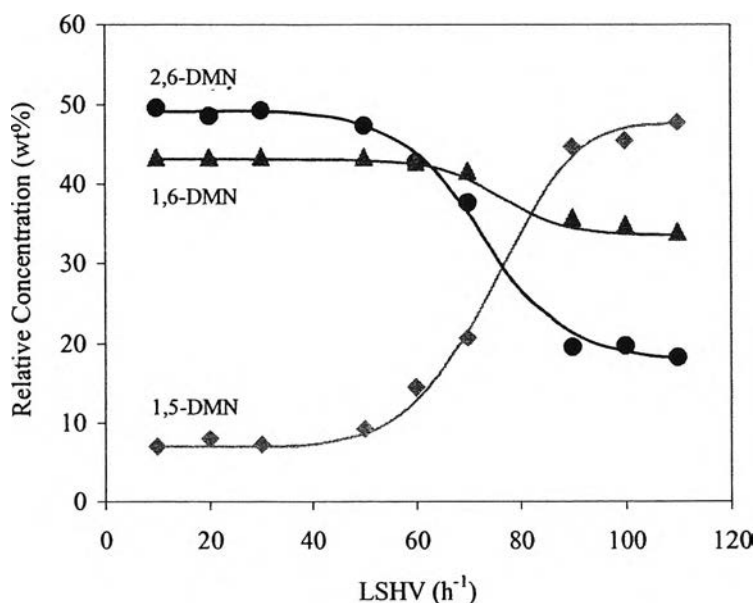


Figure 5.1 DMN distribution profiles as a function of LHSV: 180°C, 10% 1,5-DMN in toluene, and H-beta catalyst.

5.4.2 Effect of Reaction Temperature

In order to compare the effect of reaction temperatures on the isomerization with and without the presence of toluene, the experiments were carried out at 160 to 200°C with a fixed feed flow rate and concentration of 30 h⁻¹ and 10 wt%, respectively. A comparison plots between the distribution of the DMNs within the 2,6-triad vs. temperature from the 10 wt% 1,5-DMN in the system with toluene and the solvent-free are illustrated in Fig. 5.2. The use of toluene as a solvent for the isomerization does not affect the shape of the profiles and maintains the selectivity towards the 2,6-triad, which is used to relatively quantify the extent of the products produced from the 2,6-triad to those from other side reactions, close to 100%. These results also substantiate our previous hypothesis that the DMN still isomerizes upon the same pathway and behaviour even in the solvent media. Moreover, significant shifts of the profiles to the lower temperatures can be observed. It seems that the use of toluene not only facilitates the fluidity of the reactant (1,5-DMN), but also lowers the temperature needed for the system to reach equilibrium.

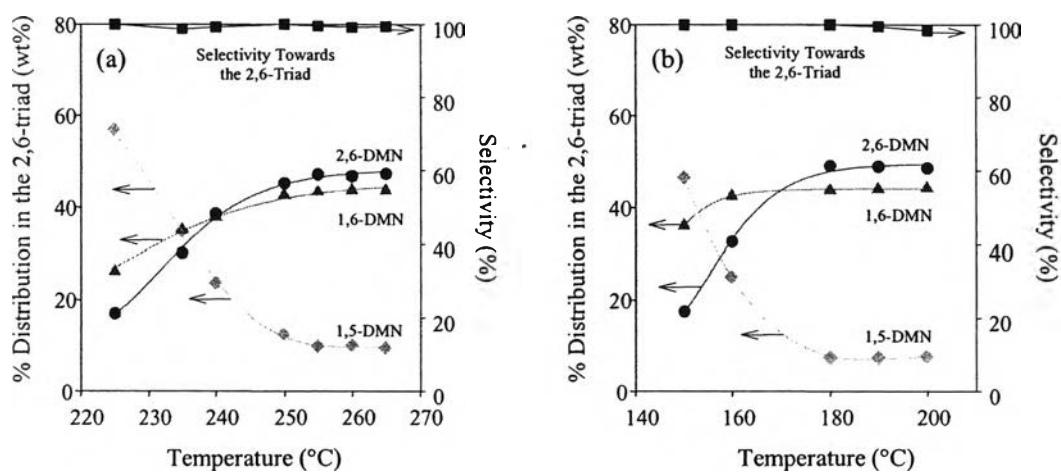


Figure 5.2 DMNs distribution within the 2,6-triad as a function of temperature (°C) from (a) solvent-free system and (b) 10% 1,5-DMN/toluene system: 30 h⁻¹ LHSV and H-beta catalyst.

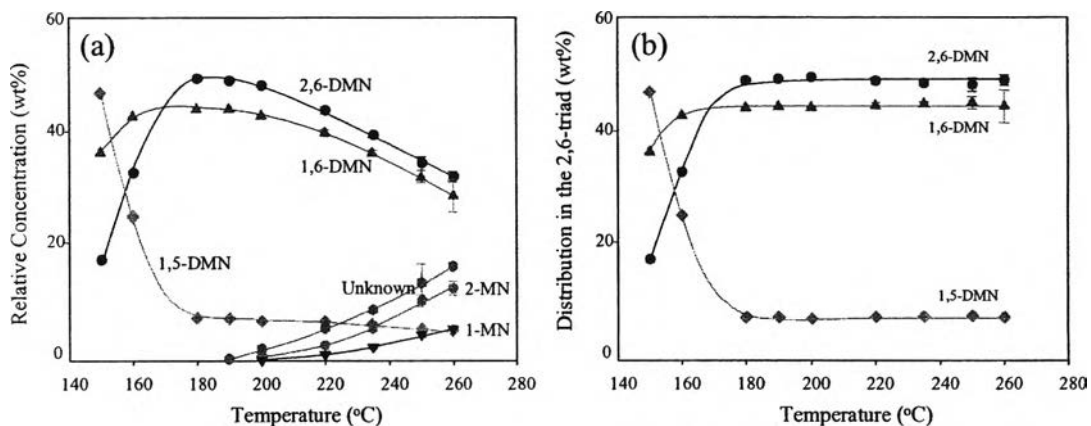


Figure 5.3 Relative concentration profiles of the products from the 10 wt% 1,5-DMN/ toluene isomerization with 30 h^{-1} LHSV and H-beta catalyst as a function of temperature; (a) of the products in the isomerized stream and (b) of the species in the 2,6-triad.

Another experiment on side products formation was subsequently conducted at the temperatures up to 265°C . As exhibited in Fig. 5.3(a), the isomerization at the temperatures higher than 180°C entails the formation of side products including 1- and 2-methylnaphthalene (MN) and unknowns. It is noted that the term “unknown” in this figure includes relatively low quantities of some DMNs outside the 2,6-triad (e.g. 2,7-DMN, 1,7-DMN, 1,8-DMN) and some light- and heavy-unknowns, expected from trans-alkylation and disproportionation. Even the concentrations of the DMNs are significantly suppressed at the high temperatures, their relative concentrations in the 2,6-triad are still conserved as illustrated in Fig. 5.3(b). This result reveals that the isomerizations are still in equilibrium even with the present of other side reactions at high temperatures. In other words, it seems that the energy applied to the system is firstly consumed by the isomerization in the 2,6-triad before the excess being utilized by other side reactions. All in all, it seems that the major side products are significantly generated after the temperature is higher than 190°C , which is higher than that required for the reaction to reach its equilibrium (180°C for 10 wt% 1,5-DMN feed, as shown in Fig. 5.2). Therefore, it can be concluded that besides the role of toluene to allow the isomerization approaching its equilibrium at significant lower temperatures, less side products

formation is another advantage from this solvent system. As a result, toluene is suggested to be possibly used as a solvent for the isomerization since it does not change the main desired reaction route, does not undergo side reactions, facilitates the reaction to reach its equilibrium at lower temperatures and suppresses side products formation under the studied conditions.

5.4.3 Effect of Feed Concentration

As toluene can expedite the isomerization towards its equilibrium, the effect of DMN concentration on the required temperature of the reaction to reach its equilibrium was then investigated. By varying the 1,5-DMN concentration from 1 wt% to that close to its solubility limit in toluene, which is 30 wt%, for the isomerization at the temperature range of 150 to 200°C and 30 h⁻¹ LHSV, identical DMN concentration profiles (Fig. 5.2) were obtained. Differences in the temperature requirements for the reaction to reach its equilibrium can only be observed when the 1,5-DMN concentration in the feed changes. These results substantiate our previous hypothesis that the change in the feed concentration by the presence of toluene shifts the reaction to lower temperature without interrupting the reaction route. Fig. 5.4 shows the correlation between the feed concentration and the required temperature for the isomerization to reach its equilibrium. Interestingly, the equilibrium compositions of the different feed concentrations at different reaction temperatures are almost identical, which is different from the results of solvent-free isomerization. In that case, the equilibrium composition is a function of temperature due to the endothermic of the isomerization. It was revealed that the required temperature decreases as a linear function of the DMN concentration. This result suggests that mass transfer of the species in the media is one of the factors controlling the isomerization under the testing condition. As expected, the use of toluene would enhance the transportation of the DMN species in the solvent media. Therefore, the lower DMN concentration, the higher toluene content, the less thermal energy required to facilitate the transportation of DMN to the catalyst. Almost 100°C of the reaction temperature can be reduced when the system is changed from a solvent-free system to that with 30 h⁻¹ LHSV of 1 wt% 1,5-DMN in toluene.

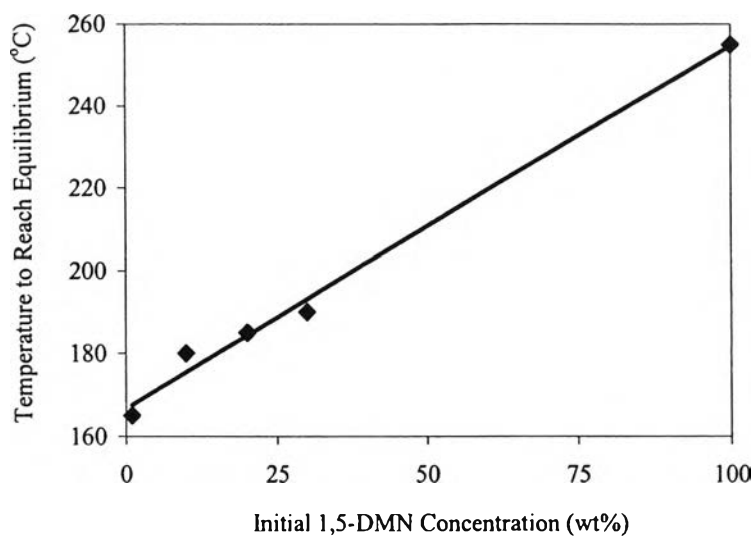


Figure 5.4 Correlation between the required temperature to reach equilibrium of 1,5- to 2,6-DMN isomerization and DMN concentration: 30 h⁻¹ LHSV and H-beta catalyst.

5.4.4 Chemical Equilibrium Consideration for the Catalytic Isomerization in Toluene

To illustrate the unexpected roles of toluene on the isomerization, equilibrium constants of the solvent system were calculated using equation (2). Table 5.1 lists the equilibrium compositions with their equilibrium constants of the solvent and solvent-free systems [4] at the temperature that the thermodynamic equilibrium can be approached. As beforehand mentioned, the isomerizations in the solvent systems provide the same equilibrium compositions even at different starting concentrations and temperatures. This interesting evidence was not observed from the solvent-free system. By performing the isomerization without solvent, the equilibrium compositions were found to strongly depend on reaction temperature, particularly for the isomerization from 1,5-DMN to 1,6-DMN [4]. The variation of the equilibrium constants with temperature is clearly illustrated in Fig. 5.5 for both solvent and solvent-free systems.

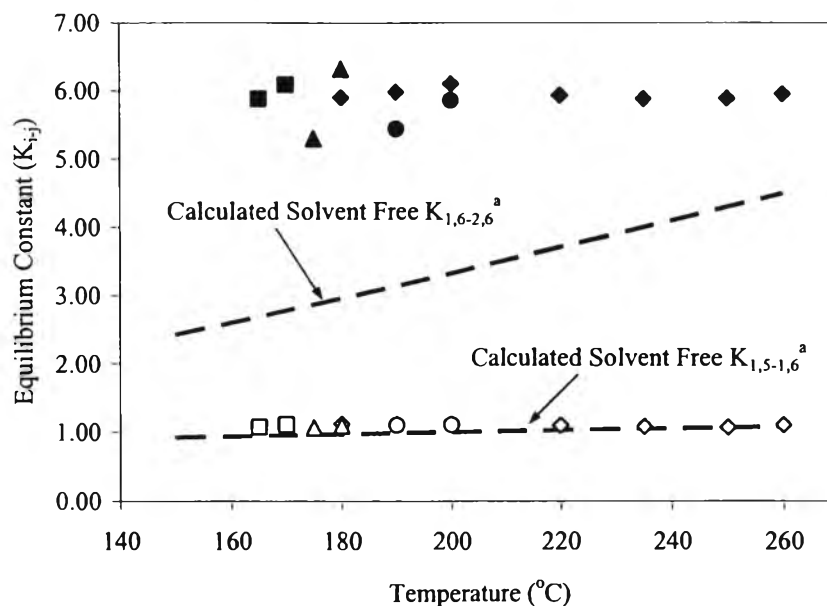


Figure 5.5 Evaluation of equilibrium constants, $K_{i,j}$, as a function of temperature for the isomerizations in the 2,6-triad with^a and without the presence of the solvent: (a) from [4], filled symbols indicate the calculated $K_{1,6-2,6}$ values while opened symbols indicate that of calculated $K_{1,5-1,6}$ from the 1 wt.% 1,5-DMN system (■, □), 10 wt.% 1,5-DMN system (◆, ◇), 20 wt.% 1,5-DMN system (▲, △) and 30 wt.% 1,5-DMN system (●, ○).

As previously discussed, feed concentration independence can be observed for both equilibrium constants of the solvent system. Moreover, the constants are, however, barely affected by temperature and the $K_{1,6-1,5}$ constant is significantly higher than those of the solvent-free system while the other constant ($K_{2,6-1,6}$) is not. These results suggest that the presence of toluene leads to the modification of the isomerization thermodynamics, particularly for the first isomerization step, probably due to the solvation of the DMN species by the solvent as frequently observed from other types of organic reaction in solvent media [11-15]. In order to depict the solvation effect on the reaction thermodynamics by the presence of toluene, the enthalpy diagram for the 1,5-DMN to 2,6-DMN isomerization in the solvent-free and toluene systems was proposed in Fig. 5.6 based on our previous calculations reported elsewhere [4] and the results of the solvent

system in this contribution. It should be noted that the modification of the reaction thermodynamics is independent of the interactions between the DMN species and the catalyst that are generally different for the solvent and solvent-free systems. As exhibited in the diagram, it is believed that the very closed dipole moment of 1,6-DMN and toluene would result in the strong interaction between the two species and the high solvation energy. Therefore, the endothermicity of the 1,5-DMN to 1,6-DMN isomerization is reduced and the isomerization is driven towards the formation of 1,6-DMN than that in the solvent-free system. Thus, the variation of the $K_{1,6-1,5}$ is significantly suppressed and the magnitude of the constant increases. In addition, the strong interaction would entail a stable profile of 1,6-DMN in toluene media as previously mentioned and observed in Fig. 5.1 and 5.2.

For the second step of isomerization, it appears that toluene does not significantly affect the reaction thermodynamics. Only a slight reduction of the reaction endothermicity is observed, resulting in the reduction of $K_{2,6-1,6}$ temperature variation while maintaining the constant magnitude. Since the presence of toluene in the catalytic isomerization resulted in the increase in the $K_{1,6-1,5}$ constant while maintaining the $K_{2,6-1,6}$ constant, the yield of 2,6-DMN from the reaction is slightly increased compared with that of the solvent-free system as observed in Table 5.1.

From the above results, the equilibrium of catalytic isomerizations could be easily reached with the presence of toluene due to the reduction of their endothermicity. This conclusion also substantiates our previous conclusion on the by-product formation. Since the isomerization has the lower endothermicity, the same extent of energy as applied to the solvent-free system would be redundant for the toluene system, leading to the formation of some by-products at the temperature that the solvent-free isomerization does not. All in all, the result suggests that a high yield of 2,6-DMN as that from the high temperature equilibrium in the solvent-free system could possibly be achieved at low temperatures by using toluene as a solvent. However, Figs. 5.2 – 5.4 show that there is a limit to which the temperature can go down before the yield of 2,6-DMN starts to decrease. So, the study to understand such limitation was conducted.

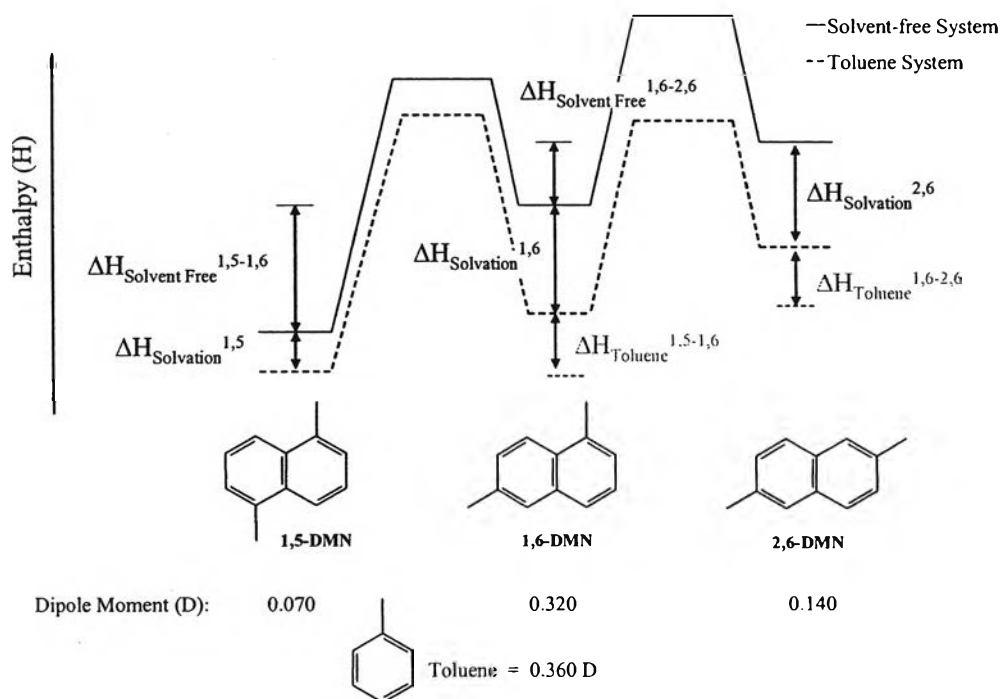


Figure 5.6 Proposed enthalpy diagram of the 1,5-DMN to 2,6-DMN isomerization in solvent-free and toluene systems.

Table 5.1 Equilibrium compositions and equilibrium constants of the solvent and solvent-free system

Feed Concentration (wt%)	Temperature (°C)	Equilibrium composition (%mass)			$K_{1,5-1,6}$	$K_{1,6-2,6}$
		1,5-DMN	1,6-DMN	2,6-DMN		
1	165	7.23	44.04	48.73	6.09	1.11
10	180	7.40	43.65	48.95	5.90	1.12
20	185	7.01	44.34	48.64	6.32	1.10
30	190	7.45	43.69	48.48	5.86	1.11
100 ^a	265	9.33	43.52	47.16	4.66	1.08

^aFrom [4].

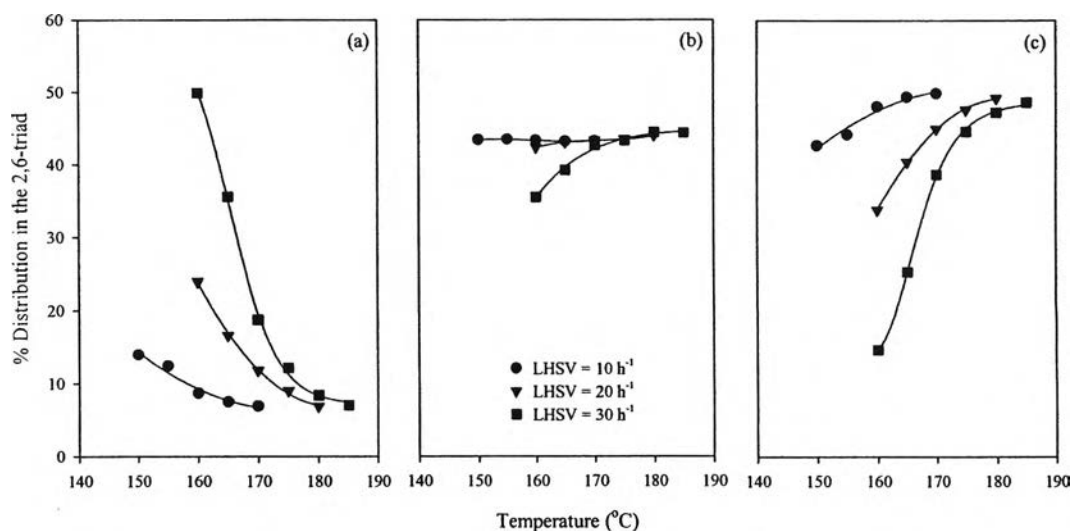


Figure 5.7 DMNs distribution within the 2,6-triad as a function of temperature (°C) of (a) 1,5-DMN, (b) 1,6-DMN and (c) 2,6-DMN: 20% 1,5-DMN/toluene system over H-beta catalyst.

Fig. 5.7 exhibits the profile of each DMN species as a function of flow rate and temperature using 20 wt% of 1,5-DMN/toluene as a feed. It was found that the similar 2,6-DMN yield can be accomplished at the lower temperatures by reducing the feed flow rate. This yield is also identical to that was produced by the 10 wt% of 1,5-DMN/toluene feed at different temperatures, which also substantiates our previous suggestion that the equilibria are barely affected by either feed concentration or temperature with the presence of toluene, and also reveals that the reaction kinetics is another controlling parameter. Performing the reaction at the high flow rate also needs more energy to rapidly drive the reactions to reach their thermodynamic equilibrium in a shorter time. Therefore, it can be concluded that the limitations to reach the maximum yield in the toluene system are mass transfer of the species due to their concentration and reaction kinetics. 2,6-DMN could possibly to be produced in a high yield as that from the high temperature equilibrium of the solvent-free system at even low temperatures even when the two mentioned restrictions have been overcome, e.g. by reducing feed concentration, increasing contact time, increasing temperature or using other higher activity catalysts.

Beside the thermodynamic effect of the solvent on the isomerization, a consideration on its effect on the reaction kinetics was also roughly made by plotting the profiles of 1,6- and 2,6-DMN as a function of 1,5-DMN conversion (Fig. 5.8). It should be noted that the maximum conversions in the figure are from different temperatures for the different systems (265°C and 180°C for the solvent-free and the toluene system, respectively). However, there is no significant difference observed as previously discussed. At any conversion below the equilibrium line, the reaction is not thermodynamically controlled; thus, the difference in the shape of the profiles could be an effect of the solvent on the reaction kinetics. Also, the maximum conversions of around 90% for the two systems are from different temperatures (265°C for the solvent-free and 180°C for the toluene system). It was found that the profile of 1,6-DMN seems to possess the higher magnitude when the isomerization is conducted in the toluene media. However, insignificant difference in the shape of 2,6-DMN profile was observed. These results suggest that the use of toluene would also increase the kinetics of 1,6-DMN formation as well.

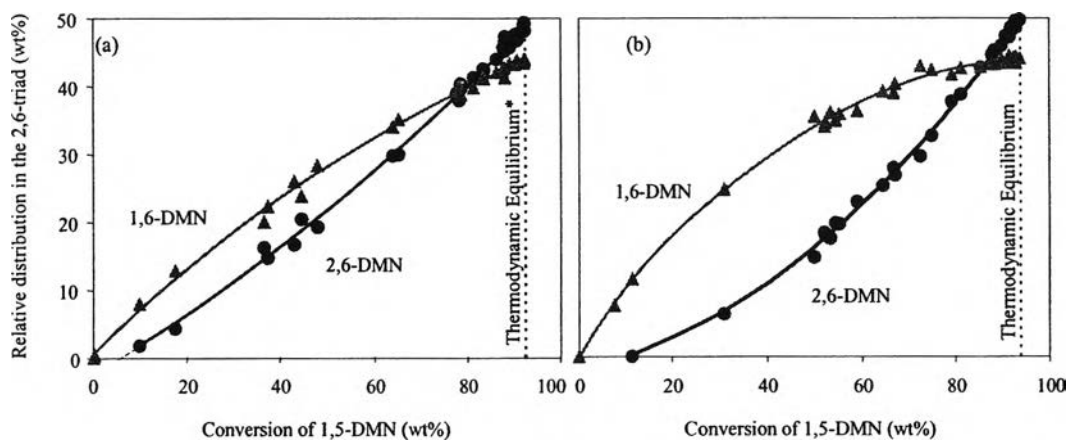


Figure 5.8 1,5- and 1,6-DMN distribution within the 2,6-triad as a function of 1,5-DMN conversion from (a) solvent-free and (b) toluene system over H-beta catalyst in which their thermodynamic equilibria are from 265 and 180°C, respectively.

5.5 Conclusions

Catalytic isomerization of 1,5-DMN to 2,6-DMN was investigated in a continuous flow fixed bed system using toluene as a solvent. As a result, the unexpected roles of using toluene as a solvent for the 1,5- to 2,6-DMN isomerization was revealed in this study. The presence of toluene does not only fluidize the solid reactant to facilitate the reaction for a continuous flow fixed bed system and enhances the system mass transfer as expected, but also expedites the reaction to reach its equilibrium at significant lower temperatures and with less side products formation by modifying the isomerization thermodynamics. As the results, 2,6-DMN could possibly be produced in a high yield as that from the high temperature equilibrium of the solvent-free system at even low temperatures when the system is not limited by mass transfer of the DMN species and the reaction kinetics.

5.6 Acknowledgements

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