ELSEVIER

Chemical Engineering Journal 114 (2005) 73–79

Chemical Engineering Journal

www.elsevier.com/locate/cej

Isomerization of 1,5- to 2,6-dimethylnaphthalene and its thermodynamic aspects

Natthakorn Kraikul[a], Pramoch Rangsunvigit[a,*], Santi Kulprathipanja[b]

[a] *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *UOP LLC, 50 East Algonquin Road, Des Plaines, IL 60017-5016, USA*

Received 1 June 2005; received in revised form 16 September 2005; accepted 23 September 2005

Abstract

Study on liquid phase isomerization of 1,5- to 2,6-dimethylnaphthalene (DMN) was conducted in a batch reactor using acidic zolite catalysts. The effect of catalyst amount, catalyst type, and reaction temperature were investigated before thermodynamic study. The results showed that H-beta zolite was the best catalyst for the reaction. Interestingly, the isomerization of 2,6-DMN from 1,5-DMN under particular conditions was not only limited by the thermodynamic equilibrium, but also by the kinetic control of the first isomerization step from 1,5-DMN to 1,6-DMN. Both restrictions should be properly manipulated in order to maximize the 2,6-DMN production. The thermodynamic study indicated an endothermic characteristic of the isomerization and provided information about thermodynamic properties of 1,5- and 1,6-DMN and equilibrium constant of the reactions that had not been reported before in literatures.

Keywords: Dimethylnaphthalenes; Isomerization; Thermodynamic; Catalysis

---

1. Introduction

2,6-Dimethylnaphthalene (2,6-DMN) has been known as an economical key intermediate for producing high-performance thermoplastic polyethylene naphthalate (PEN) due to its high reactivity and selectivity to be further synthesized without carbon losses [1,2]. Superior properties of PEN is expected to drive the material demand for innovative applications but that has been outweighed by its cost disadvantages coming from complex and multiple steps synthesis, particularly for the 2,6-DMN production [3]. Presently, only commercial large-scale production (30 kt/year) patented by BP-Amoco has claimed the success in the 1,5-DMN production with the high 90s conversion and selectivity [4]. However, the final isomerization step from 1,5- to 2,6-DMN of the process is still thermodynamically limited leading to the low availability and high production cost of 2,6-DMN [3].

The overall possible isomerization pathways of DMNs are shown in Fig. 1. Based on the thermodynamic and chemistry of methyl group migration, the isomerization of 10 DMN isomers can be divided into three different groups, each called triad, and an additional single isomer depends on the ease of isomerization. Therefore, only two DMN isomers (1,5- and 1,6-DMN) are beneficial since they can be effectively isomerized to be the profitable 2,6-DMN while other seven DMN isomers cannot. On the other hand, losses of DMNs from the 2,6-triad by inter-triad isomerization also mean the lost of profit.

Until now, only few studies have been conducted for the DMN isomerization [6–8], especially within the 2,6-triad. Moreover, there is no thermodynamic study of the reaction reported in literatures. Almost former studies have been distributed as patents and only focused on the yield of 2,6-DMN achieving from a claimed condition. The most intensively claimed zeolite was mordenite [7,9–11]. In addition, BP Amoco also claimed beta zeolite as the highest efficiency catalyst [4,12].

In this contribution, liquid phase isomerization of DMN was studied using 1,5-DMN as a reactant with the focus on 2,6-DMN as a desired product. Both preliminary catalysis and thermodynamic studies were emphasized to understand the reaction. Studies on effect of catalyst amount, catalyst type and reaction temperature were first investigated. Subsequently, in order to understand the intrinsic thermodynamic limitations of the reaction, a thermodynamic study was also carried out.

---

[*] Corresponding author. Tel.: +66 2 218 4135; fax: +66 2 215 4459.
E-mail address: Pramoch.R@chula.ac.th (P. Rangsunvigit).

1385-8947/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2005.09.011

Nomenclature

a, b, c	coefficient of molar heat capacity expression
Δa	$\sum \nu_i a_i$
Δb	$\sum \nu_i b_i$
Δc	$\sum \nu_i c_i$
$C^0_{\mathrm{P},i}$	molar heat capacity of component i in the liquid phase
ΔG°_{i-j}	standard Gibbs free energy change of isomerization from i to j (cal mol^{-1})
ΔH°_{i-j}	standard enthalpy change of isomerization from i to j (cal mol^{-1})
I, I'	integration constant
$K_{i\text{–}j}$	thermodynamic equilibrium constant of reactant i to product j isomerization
$K_{1,5\text{–}1,6}$	thermodynamic equilibrium constant of 1,5-DMN to 1,6-DMN isomerization
$K_{1,6\text{–}2,6}$	thermodynamic equilibrium constant of 1,6-DMN to 2,6-DMN isomerization
ΔS°_{i-j}	standard entropy change of isomerization from i to j (cal mol^{-1} K^{-1})
T	absolute temperature (K)

Greek letters

α	mole fraction of DMNs distributed in the 2,6-triad at equilibrium
ν_i	stoichiometric coefficient of component i

Subscripts

i	of reactant i
j	of product j
p	in terms of pressure

Superscripts

$\circ$	of standard condition at 298 K and atmospheric pressure

2. Experimental

2.1. Catalyst preparation

Acidic catalysts used in this study were H-beta (24 SiO_2/Al_2O_3, 25% alumina binder, UOP LLC, USA), H-mordenite (20 SiO_2/Al_2O_3, 30% alumina binder, UOP LLC, USA), and H-ZSM5 (20 Si/Al 20% alumina binder, UOP LLC, USA). Prior to the study, all catalysts were ground, sieved to be in the range of 20–40 mesh, and calcined at 500 °C for 3 h.

2.2. Experimental apparatus

2.2.1. Reactor

All isomerization experiments of 1,5-dimethylnaphthalene (1,5-DMN) were carried out in a quartz 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.

2.2.2. Analytical method

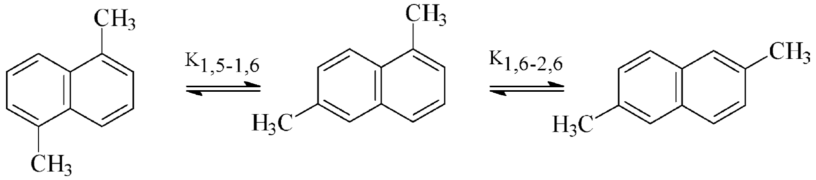
A sampled product of around 0.3 g from each isomerization reaction was dissolved in 2 ml of toluene to be a representative sample of the testing condition. The solution was manually injected into a HP gas chromatograph (GC) equipped with Carbowax® 20 m (Supelco 2-4085) capillary column that can separate 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.

2.3. Experimental procedure

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 to 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 1 h, 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 1 h.

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 as the following:



(1)

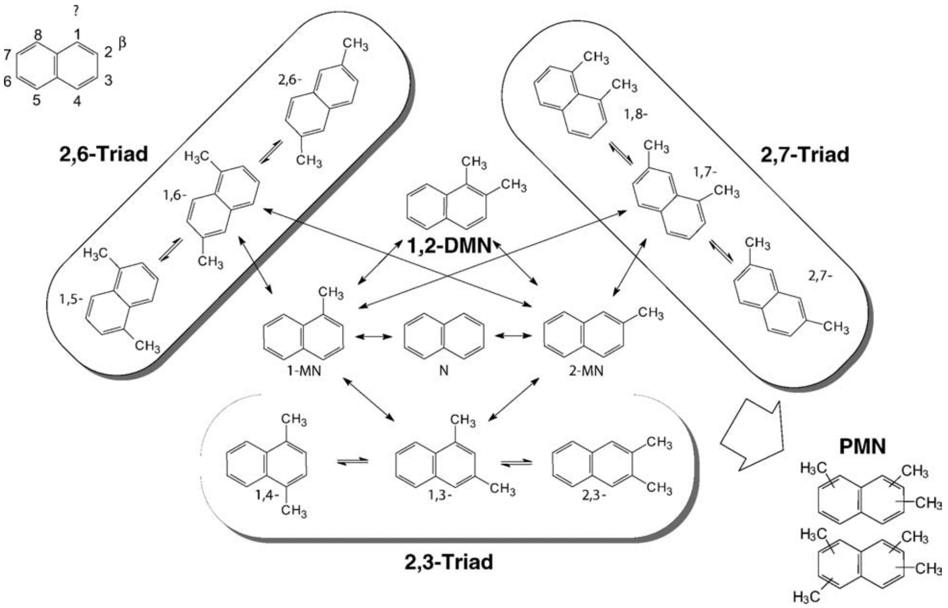


Fig. 1. Schematic diagram representing isomerizations among 10 DMN isomers (modified from [5]).

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.

With the ideal solution assumption, i.e., the equilibrium constant, K, of 1,5-DMN isomerization to 1,6-DMN ($K_{1,5\text{–}1,6}$) and 1,6-DMN isomerization to 2,6-DMN ($K_{1,6\text{–}2,6}$) can be defined as

$$K_{i-j} = \frac{\alpha_j}{\alpha_i}. \tag{2}$$

Relationship between temperature and equilibrium constant can be described using the Gibbs–Helmholtz equation,

$$\ln K_{i-j} = \frac{\Delta S^\circ_{i-j}}{R} - \frac{\Delta H^\circ_{i-j}}{R}\frac{1}{T}. \tag{3}$$

By plotting $\ln K_{i-j}$ versus $1/T$, the changes in standard enthalpy, and entropy can be estimated. The standard Gibbs free energy change, ΔG°_{i-j}, can then be estimated by its definition of $\Delta G = \Delta H - T\Delta S$. The standard enthalpy and entropy of 1,5-DMN and 1,6-DMN were also calculated from the enthalpy, entropy, and Gibbs free energy of formation reported by Richard and Helgeson [13] using the following equations:

$$\Delta H^\circ = \sum_i \nu_i \Delta H^\circ_{\mathrm{f},i}, \tag{4}$$

$$\Delta S^\circ = \sum_i \nu_i \Delta G^\circ_{\mathrm{f},i}, \tag{5}$$

$$\Delta G^\circ = \sum_i \nu_i \Delta G^\circ_{\mathrm{f},i}, \tag{6}$$

The Van't Hoff equation is also used to account for the change in temperature from the standard condition to the reaction temperature,

$$\frac{\mathrm{d}(\ln K_{i-j})}{\mathrm{d}T} = \frac{\Delta H}{RT^2}. \tag{7}$$

For liquid phase, a general expression for the heat of reaction can be expressed as

$$\Delta H = \Delta H^\circ + \int_{298}^{T} \Delta C^\circ_{\mathrm{P}}\,\mathrm{d}T \tag{8}$$

with

$$\Delta C^\circ_{\mathrm{P}} = \sum_i \nu_i C^\circ_{\mathrm{P},i}. \tag{9}$$

Integrating Eq. (8) with $C_{\mathrm{P}} = a + bT + cT^{-2}$ yields the below polynomial equation

$$\Delta H = I + (\Delta a)T + \frac{\Delta b}{2}T^2 - \frac{\Delta c}{T} \tag{10}$$

Substitution Eq. (10) into Eq. (7) and subsequent integration yield

$$\ln K_{i-j} = \left(-\frac{I}{RT} + \frac{\Delta a}{R}\ln T + \frac{\Delta b}{2R}T + \frac{\Delta c}{2RT^2}\right) + I'. \tag{11}$$

Experimental data fitting gives the value of Δa, Δb, and Δc. With the reported value of a, b, and c for 2,6-DMN by Richard and Helgeson [13], the value of a, b, and c for 1,5-DMN and 1,6-DMN can also be estimated.

3. Results and discussion

3.1. Effect of catalyst amount

Amount of H-beta catalyst was varied from 1 to 5 wt.% and tested for the isomerization activity at 265 °C for 1 h under atmospheric pressure. The results, as illustrated in Fig. 2, show that the amount of the catalyst used has an effect on the DMNs distribution and selectivity. The amount of 1,5-DMN converted to the desired isomer, 2,6-DMN, is small with the amount of the

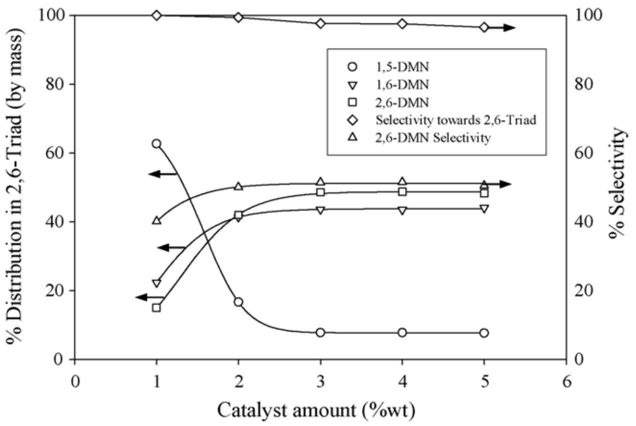


Fig. 2. DMNs distribution and selectivity in the 2,6-triad as a function of catalyst amount (wt.%) at 265 °C, 1 atm and 1 h of reaction time.

catalyst lower than 3 wt.%. That may be due to the result of insufficient active site available. When the amount of the catalyst is higher than 3 wt.%, higher amount of 2,6-DMN produced can be observed and reaches its maximum at 48% (distributed in its triad). This is also consistent with results reported to be the equilibrium limitation in literatures [1,4,12]. Even though using the catalyst in much higher amount does not affect the 2,6-DMN selectivity, it results in lower selectivity towards the 2,6-triad route. On the other hand, higher loss of valuable DMNs to other irrecoverable isomers as well as undesired products increases with the increase in the catalyst amount. The major undesired products are 1- and 2-methylnaphthalene and some undefined heavies. Therefore, 3 wt.% of a catalyst was selected to be the optimal amount on both conversion and selectivity.

3.2. *Effect of catalyst type*

Three different acidic catalysts (H-beta, H-mordenite and H-ZSM5) were investigated for their isomerization activity at 265 °C with fixed amount of 3 wt.%. Fig. 3 demonstrates product distribution achieved from the different acidic catalysts used. Five main species were detected in the isomerization product, which are 1,5-DMN, 1,6-DMN, 2,6-DMN, methylnaphthalene (MN) and polymethylnaphthalene (PMN). The first three DMN isomers are the product from the isomerization that proceeds through the desired 2,6-triad, whereas the last two are side products (as shown in Fig. 1). Since the isomerization from 1,5- to 2,6-DMN cannot be executed without producing 1,6-DMN, the catalyst that can catalyze 1,5-DMN to 2,6-DMN also facilitates the formation of 1,6-DMN. Under the testing condition, both H-beta and H-mordenite catalysts catalyze the reaction and 1,6-DMN was also observed. However, only the reactions catalyzed by the H-beta catalyst reach their thermodynamic equilibrium. The H-mordenite catalyst can also catalyze the reaction under this testing condition but to a lesser extent than the H-beta catalyst while the H-ZSM5 catalyst cannot; thus only 1,5-DMN was observed. These results can be explained by differences in diffusion energy barrier of 1,5-DMN, 1,6-DMN, and 2,6-DMN through different zeolite pore structures. Millini et al. reported that the diffusion of 1,5-DMN into the MFI pore structure (H-ZSM5) needs very high energy (747.6 kJ mol^{-1}) than that of MOR (mordenite) and *BEA (beta) (12.1 and 34.7 kJ mol^{-1}, respectively) [6]. For *BEA and MOR, since their computed energy barriers are quite the same, the difference in the activity is probably due to the result of the pore dimensional differences. The three-dimensional *BEA pore structure facilitates the reaction much faster than the one-dimensional pore structure of MOR, and results in the higher conversion. Therefore, among the tested catalysts, the H-beta zeolite was selected for further study.

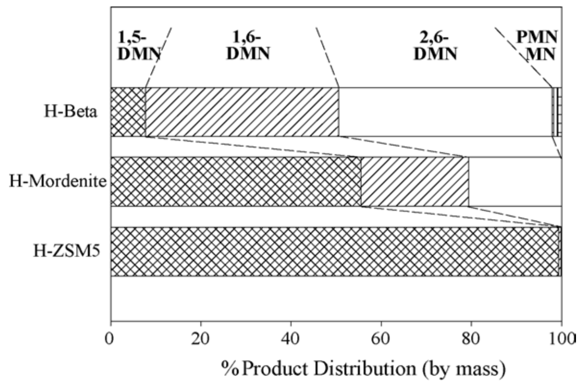


Fig. 3. DMNs distribution and selectivity towards the 2,6-triad as a function of catalyst type at 265 °C, 1 atm and 1 h of reaction time (MN: methylnaphthalene, DMN: dimethylnaphthalene, PMN: polymethyl-naphthalene).

3.3. *Effect of reaction temperature*

H-beta zeolite as a catalyst was used in this study with 3 wt.% with respect to the weight of 1,5-DMN as recommended from the previous two experiments. The isomerization reaction was carried out under atmospheric pressure at the temperatures of 175, 200, 225, 235, 250, 255, and 265 °C. Effect of temperature on the product distribution is shown in Fig. 4. 1,5-DMN is converted to 1,6-DMN and 2,6-DMN in much higher amount when the temperature increases. This result is easily explained by the fact that the reaction rate is increased as the temperature increases for the kinetic controlled reaction. Interestingly, at the temperature higher than 255 °C, the amount of 2,6-DMN

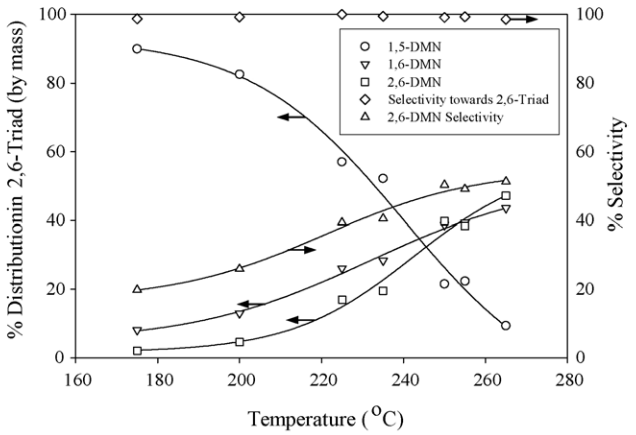


Fig. 4. DMNs distribution and selectivity in the 2,6-triad as a function of temperature under 1 atm, 1 h of reaction time, and 3 wt.% of H-beta catalyst.

is higher than that of 1,6-DMN and reaches its equilibrium limit of around 48% (in 2,6-triad) at 265 °C. This result indicates that a temperature higher than 255 °C is required to drive the reaction approaching its equilibrium limitation within 1 h of reaction time.

The selectivity of 2,6-DMN is low at low temperatures because 1,5-DMN is still predominately isomerized to 1,6-DMN, which is not immediately further isomerized to 2,6-DMN. A significant increase in the 2,6-DMN selectivity at the higher temperature also evidences the further isomerization of 1,6-DMN to 2,6-DMN. Interestingly, the selectivity towards the 2,6-triad is hardly affected by the temperature. It means that the increase in the reaction temperature mainly increases the rate of the reactions towards the 2,6-triad. In other words, it seems that increasing the temperature only accelerates the isomerization of 1,5-DMN to 1,6-DMN and 2,6-DMN without facilitating other side reactions.

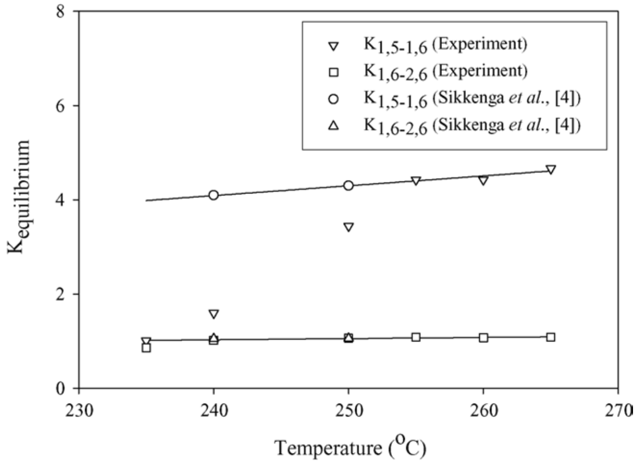


Fig. 5. Evaluation of equilibrium constants, $K_{\text{equilibrium}}$, as a function of temperature for the reactions in the 2,6-triad.

3.4. Thermodynamic study

By carrying out the isomerization reaction at different temperatures until the DMNs distribution does not change with reaction time, the amount of each DMN isomer distributed inside the 2,6-triad were estimated as reported in Table 1. Maximum conversion of 1,5-DMN of around 90% was obtained from the reaction carried out at 255–265 °C. In addition, differences in the product distribution from that reported by Sikkenga et al. [4] were observed for the reaction below 255 °C, meaning lower activity of the employed H-beta zeolite to catalyze the reaction below the temperature.

Equilibrium constants for the isomerization of 1,5-DMN to 1,6-DMN ($K_{1,5\text{–}1,6}$) and 1,6-DMN to 2,6-DMN ($K_{1,6\text{–}2,6}$) were calculated using Eq. (2) and plotted as a function of temperature as shown in Fig. 5. The increment of the equilibrium constants with increasing temperature indicates the endothermic characteristics of the reactions. By comparing the estimated equilibrium constants in this study to the calculated ones from Sikkenga et al. [4], the values of $K_{1,6\text{–}2,6}$ estimated from the experimental data at temperatures above 240 °C are almost identical and show the same trend as that calculated from the literature data, while the values of $K_{1,5\text{–}1,6}$ are not. Apparently, the estimated values of $K_{1,5\text{–}1,6}$ in this study are much lower than the calculated ones from the literature data and also deviate from the equilibrium trend when the temperature is below 255 °C.

The results reveal an interesting behavior of the reactions in the 2,6-triad, i.e. the isomerization rate from 1,6-DMN to 2,6-DMN is much higher than that of 1,5-DMN to 1,6-DMN. In other words, the isomerization of 1,6-DMN to 2,6-DMN rapidly takes place and thermodynamically controlled at all testing temperatures while the isomerization of 1,5-DMN to 1,6-DMN is still kinetically controlled below 255 °C.

Fig. 6 illustrates ratios of 1,6-DMN to 1,5-DMN and 2,6-DMN to 1,6-DMN calculated from the result at 1 h reaction time. The dashed and dotted lines are used to represent the estimated $K_{1,5\text{–}1,6}$ and $K_{1,6\text{–}2,6}$ from this work, respectively. It is obvious that the equilibrium limitation can be reached within 1 h reaction time for the isomerization of 1,6-DMN to 2,6-DMN above 250 °C, and for 1,5-DMN to 1,6-DMN isomerization at 265 °C. These results substantiate that the isomerization of 1,5-DMN to 1,6-DMN is the kinetically limiting step for producing 2,6-DMN from 1,5-DMN. Increasing the temperature above 260 °C or performing the reaction more than 3 h above 250 °C could lead the reaction from kinetically controlled to thermodynamically controlled one. Therefore, proper manipulations both kinetic control

Table 1
Composition of DMNs distributed in the 2,6-triad

Temperature (°C)	Reaction time (h)	Equilibrium composition (mass%)			Equilibrium conversion (%)	$K_{1,5\text{–}1,6}$	$K_{1,6\text{–}2,6}$
		1,5-DMN	1,6-DMN	2,6-DMN			
235	6.0	34.79	35.10	30.11	65.21	1.009	0.858
240	6.5	23.67	37.79	38.54	76.33	1.597	1.020
240[a,b]	3.0	10.63	43.55	45.82	89.07	4.097	1.052
250	4.0	12.36	42.53	45.11	87.64	3.441	1.061
250[a,c]	3.0	10.13	43.59	46.28	89.53	4.301	1.062
255	3.0	9.77	43.23	46.99	90.23	4.425	1.087
260	3.0	9.83	53.51	46.66	90.17	4.426	1.072
265	1.0	9.33	43.52	47.16	90.67	4.665	1.084

[a] Calculated from the presented data of US Patent 4,962,260 (1990).

[b] Using unsupported H-beta of 30 Si/Al_2 ratio.

[c] Using H-beta of 30 Si/Al_2 ratio with 20% alumina binder.

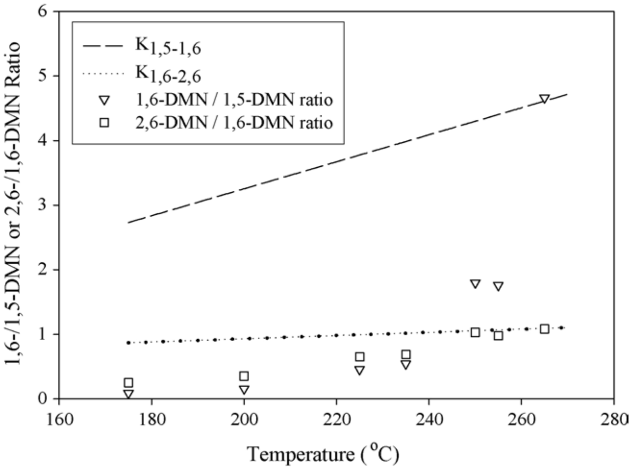


Fig. 6. Evaluation of 1,6-DMN/1,5-DMN and 2,6-DMN/1,6-DMN ratios (at 1 h of reaction time) and equilibrium constant as a function of temperature for the reactions in the 2,6-triad.

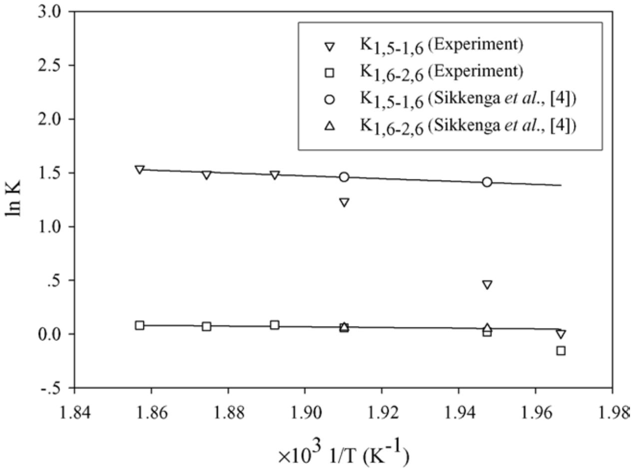


Fig. 7. Equilibrium constants represented in the Van't Hoff coordinates for DMN isomerization in the 2,6-triad.

of 1,5-DMN isomerization to 1,6-DMN and thermodynamic control of the two-step isomerizations are the crucial aspect to maximize the production yield of 2,6-DMN.

A plot of equilibrium constants versus temperature in the Van't Hoff coordination following Eq. (3) is shown in Fig. 7. By fitting the Gibbs–Helmholtz equation to the data using nonlinear regression method of SigmaPlot 2000, the following equilibrium correlation can be obtained

$$\ln K_{1,5-1,6} = 3.872 - \frac{1263}{T} \tag{12}$$

$$\ln K_{1,6-2,6} = 0.6746 - \frac{319.5}{T} \tag{13}$$

Fitting Eq. (11) to the experimental data using the same method yields another set of relationship between equilibrium constant and reaction temperature

$$\ln K_{1,5-1,6} = 3.7812 + \frac{1438.3}{T} - 1.9980 \ln T + 0.0142T \tag{14}$$

$$\ln K_{1,6-2,6} = 0.6984 + \frac{10265}{T} - 7.2445 \ln T - 0.0485T \tag{15}$$

Based on Eqs. (3), (12), and the definition of Gibbs free energy that $\Delta G = \Delta H - T\Delta S$ along with the reported thermodynamic properties of 2,6-DMN by Richard and Helgeson [13], ΔG°, ΔS°, and ΔH° of the two isomerization reactions and the $\Delta G^{\circ}_{\mathrm{f}}$, $\Delta S^{\circ}_{\mathrm{f}}$, and $\Delta H^{\circ}_{\mathrm{f}}$ of each species can be calculated as shown in Table 2. The properties are also listed in Table 3 along with those of the other DMN isomers reported in literature [13].

Comparisons between the thermodynamic properties in Table 2 between the isomerizations of 1,5 -to 1,6-DMN and 1,6- to 2,6-DMN show that the former isomerization has more endothermicity than that of the latter. Therefore, the 1,6- to 2,6-DMN isomerization could proceed much faster than the other isomerization.

For the standard Gibbs free energy and entropy of formation of 1,5 -and 1,6-DMN estimated in this study as listed in Table 3, the results are in good agreement with those of other DMN-isomers calculated using group contribution by

Table 2
Thermodynamic properties of the isomerization reactions in the 2,6-triad

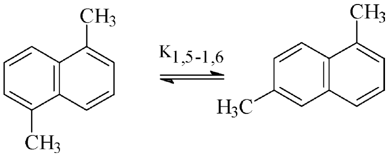
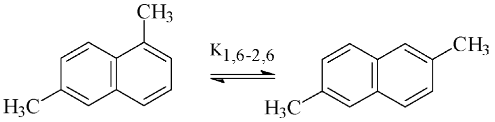
Reaction	ΔG° (cal mol^{-1})	ΔH° (cal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})
1. Isomerization of 1,5-DMN to 1,6-DMN 	216.9	2509	7.69
2. Isomerization of 1,6-DMN to 2,6-DMN 	235.4	634.9	1.34

Table 3
Summary of liquid DMNs thermodynamic properties at 25 °C and 1 atm

Compound	Caloric coefficient (cal mol^{-1} K^{-1}); $C_P^0 = a + bT + cT^{-2}$			ΔG_f° (cal mol^{-1})	ΔH_f° (cal mol^{-1})	ΔS_f° (cal mol^{-1} K^{-1})
	a (cal mol^{-1} K^{-1})	$b \times 10^3$ (cal mol^{-1} K^{-2})	$c \times 10^{-5}$ (cal K mol^{-1})			
1,2-DMN[a]	24.73	119.7	1.852	44873	4608	68.81
1,3-DMN[a]	26.82	111.9	0.000	44096	3831	68.81
1,4-DMN[a]	28.72	107.0	0.000	43994	4030	69.82
1,5-DMN[b]	43.29	253.2	0.000	43745	487	58.77
1,6-DMN[b]	39.32	309.6	0.000	43963	2997	66.46
1,7-DMN[c]	n/a	n/a	n/a	n/a	n/a	n/a
1,8-DMN[a]	24.45	121.0	0.000	51392	10009	65.06
2,3-DMN[a]	22.83	124.6	1.852	44975	4409	67.80
2,6-DMN[a]	24.92	116.8	0.000	44198	3632	67.80
2,7-DMN[a]	24.92	116.8	0.000	44198	3632	67.80

[a] Calculated using group contribution models by Richard and Helgeson (1998).
[b] Estimated in this study.
[c] No literature report.

Richard and Helgeson [13]. However, the estimated standard enthalpy of formation of 1,5-DMN is interestingly much lower than that of the others due to a large magnitude of $\Delta H^\circ_{1,5\text{–}1,6}$ evaluated from the experiments. This result also supports the fact that 1,5-DMN is easily synthesized, thus also claimed as a starting material to synthesize 2,6-DMN in many patents [4,7,9–12].

4. Conclusions

Isomerization of 1,5-DMN was studied using acidic zeolite catalysts in a batch reactor. Preliminary studies on the effect of catalyst amount, catalyst type and reaction temperature were conducted before the thermodynamic study. The results indicated that H-beta zolite was the best catalyst for the reaction. Moreover, it was found that the 2,6-DMN production from 1,5-DMN was not only limited by the thermodynamic equilibrium, but also by the kinetic control of the first isomerization step from 1,5-DMN to 1,6-DMN. Proper manipulations both restrictions are crucial to maximize the production of 2,6-DMN. In addition, the thermodynamic study provided the thermodynamic properties of these DMNs and the equilibrium constant of the reactions that have not been reported before in literatures.

Acknowledgements

Financial supports from the Ph.D. Royal Golden Jubilee Program, Thailand Research Fund, Petrochemical and Environmental Catalysis Research Unit under Ratchadapisek Somphot Endowment, PTT consortium, and The Petroleum and Petrochemical College, Chulalongkorn University are appreciated.

References

[1] L.D. Lillwitz, Production of dimethyl-2,6-naphthalenedicarboxylate: precursor to polyethylene naphthalate, Appl. Catal. A-Gen. 221 (2000) 337–358.

[2] S.B. Pu, T. Inui, Synthesis of 2,6-dimethylnaphthalene by methylation of methylnaphthalene on various medium and large-pore zeolite catalysts, Appl. Catal. A-Gen. 146 (1996) 305–316.

[3] Chem Systems, 2,6-dimethylnaphthalene (2,6-DMN): 99/00S7, Chem Systems Report, 2000.

[4] D. Sikkenga, I.C. Zaenger, G.S. Williams, Preparation of a dimethylnaphthalene, US Patent 4,962,260 (1990).

[5] R. Millini, Molecular modeling in chemical catalysis. Training course in molecular design and computer-assisted combinatorial chemistry, ICS-UNIDO, Area Science Park, Trieste, Italy, 5–8 July 2004.

[6] R. Millini, F. Frigerio, G. Bellussi, G. Pazzuconi, C. Perego, P. Pollesel, U. Romano, A priori selection of shape-selective zeolite catalysts for the synthesis of 2,6-dimethylnaphthalene, J. Catal. 217 (2003) 298–309.

[7] I. Ferino, R. Monaci, L. Pedditzi, E. Rombi, V. Solinas, Isomerization of dimethylnaphthalene over zeolites, React. Kinet. Catal. L. 58 (1996) 307–314.

[8] S.B. Pu, T. Inui, Influence of crystallite size on catalytic performance of HZSM-5 prepared by different methods in 2,7-dimethylnaphthalene isomerization, Zeolites 17 (1996) 334–339.

[9] M. Takagawa, R. Shigematsu, K. Nagagata, Method for isomerizing dimethylnaphthalene, US Patent 5,495,060 (1996).

[10] P.T. Barger, T.J. Barder, D.Y. Lin, S.H. Hobbs, Continuous process for the production of 2,6-dimethylnaphthalene, US Patent 5,004,853 (1991).

[11] J.K. Allen, R.J. Bertolaini, Process for the isomerization of dimethylnaphthalenes using a mordenite/alumina catalyst, US Patent 4,041,089 (1997).

[12] D. Sikkenga, I.C. Zaenger, G.S. Williams, Preparation of a dimethylnaphthalene, US Patent 5,118,892 (1992).

[13] L. Richard, H.C. Helgeson, Calculation of the thermodynamic properties at elevated temperatures and pressures of saturated and aromatic high molecular weight solid and liquid hydrocarbons in kerogen, bitumen, petroleum and other organic matter of biogeochemical interest, Geochim. et Cosmochim. Acta 62I (1998) 3591–3636.