CHAPTER VII
INTEGRATIONS OF CATALYTIC ISOMERIZATION TO ADSORPTIVE SEPARATION FOR THE PRODUCTION OF HIGH PURITY 2,6-DIMETHYLNAPHTHALENE*

7.1 Abstract

In this study, an alternative non-energy intensive system for the production of 2,6-DMN (catalytic isomerization in a solvent media and adsorptive purification) was investigated using the pulse test technique. The integrations of the isomerization to the adsorption were accomplished in two different approaches; subsequent adsorption after the isomerization and the reactive adsorption based technique. By subsequently connecting the adsorption unit after the isomerization with the selected adsorbent, catalyst and desorbent, the system shows a potential for producing high purity 2,6-DMN. Moreover, the results also suggest a possibility to enhance the overall productivity of 2,6-DMN by separating the chemical from the product stream during the isomerization. However, the results from the reactive adsorption study indicate only a narrow possible operating window for the high purity 2,6-DMN production. Carrying out the system at the temperatures that the isomerization can reach its equilibrium entails the reduction in either the 2,6-DMN separation due to the very fast in the reaction kinetics or the 2,6-DMN yield by the backward isomerization from 2,6- to 1,6- and 1,5-DMN. On the other hand, operating the system below the equilibrium of the isomerization at appropriate temperatures is only a possible approach to produce high purity 2,6-DMN using the reactive adsorption technique.

## 7.2 Introduction

As civilization draws many innovative applications to polyesters, demands for engineering plastics are expected to be substantially increased in near future. Polyethalene naphthalate (PEN) is one of the plastics offering superior properties than other thermoplastic polyesters, particularly for the conventionally used polyethylene terephthalate (PET) [1-2]. However, lowering its production cost is still crucial for the PEN demand to breakthrough the polyesters market [2]. One of the parameters that currently determines the price of PEN is the price of 2,6-dimethylnaphthalene (2,6-DMN) that is the precursor for the production. Presently, only the process of BP Amoco shows the most benefit for a large scale production (30 kt/year) of 2,6-DMN [2-3]. The process is based on the complex aromatic/olefin cyclization using *o*-xylene and butadiene as a feedstock. Four reaction-in-series, starting from alkylation, cyclization, dehydrogenation and isomerization, are employed to synthesize 2,6-DMN. From the first three reaction steps, 1,5-DMN is claimed to be produced with the high 90s conversion and selectivity [2-3]. However, its subsequent isomerization into 2,6-DMN is thermodynamically controlled, to which only 48% 2,6-DMN can be produced [1-4]. Finally, freeze crystallization as a 2,6-DMN purification means is conducted to increase the purity to be higher than 90% as the industrial requirement [5-6]. As a result, the low ability as well as the high utility used for the synthesis create the high cost of 2,6-DMN, which limits the large scale production and commercialization of PEN [2]. On the other hand, it seems that if any developments that offer the higher product yield of 2,6-DMN from the isomerization as well as the lower in either the process complexity or utility requirement can be established, the market of PEN would be potentially promoted.

Catalytic isomerization to 2,6-DMN proceeds through the equation (1) called the 2,6-triad. The best catalyst for this reaction is H-beta catalyst that facilitates the formation of 2,6-DMN at lower temperatures than other zeolites [1-4]. However, the reaction still needs to be carried out at least 250°C in order to get the most benefit from the maximum yield of 2,6-DMN at high temperature equilibrium. Recently, an alternative to produce 2,6-DMN in a high yield at low temperatures via its isomerization over H-beta catalyst in toluene media was reported [7]. This result

reveals a possibility that a new process utilizing the lower energy than the conventional one could be demonstrated. Moreover, another report also shows the success of using adsorption technique for the 2,6-DMN purification as an alternative non-energy intensive approach [8]. Therefore, a new energy-effective process would be demonstrated by the integration of these two units for the production of high purity 2,6-DMN.

$$(1)$$
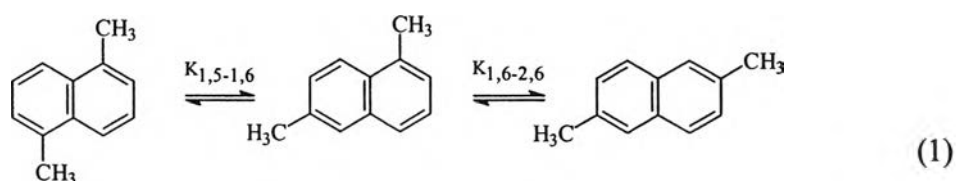
The propose of this contribution is to investigate the possibility of an alternative non-energy intensive system for producing 2,6-DMN by using the catalytic isomerization in a solvent media with the adsorptive purification. Two different integration approaches are of interest, which are the subsequent adsorption right after the isomerization and the reactive adsorption based technique. The first approach is simple and conventionally used for many high purity chemical productions. However, it is considered to be an alternative from the conventional large scale process of BP Amoco (as shown in Fig. 7.1). For the reactive adsorption approach, its uniqueness in the combination of reaction and adsorption into a single unit has been proven to provide a smaller inventory, compactor plant layout, better energy management and greater throughput by a shift of the reaction product composition beyond the equilibrium due to *in situ* adsorption [9-13]. Hence, it is very challenging to conduct the isomerization to 2,6-DMN that is controlled by thermodynamic equilibrium using such the technique. Firstly, the isomerization and adsorption over a selected catalyst and adsorbent were individually studied. After that, experiments on the integration of isomerization to the adsorption were conducted. The results from both individual and integration studies were also compared to understand the alternative systems.
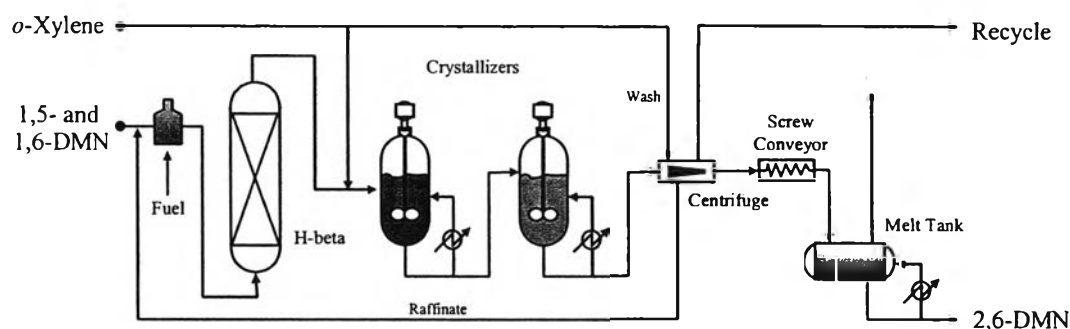
Figure 7.1 Schematic diagram of the isomerization and crystallization for producing 2,6-dimethylnaphthalene by BP Amoco process (redrawn from [2]).

7.3 Experimental

Before studying the production of 2,6-DMN using the integrated systems of isomerization and adsorption, the two processes were individually studied using the pulse test technique with the experimental setup illustrated in Fig. 7.2. For the isomerization study, acidic beta zeolite (24 SiO_2/Al_2O_3, 25% alumina binder, UOP LLC, USA) as a catalyst was packed into a 3 mL stainless steel reactor before subsequently filling 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% 1,5-DMN (96%, Aldrich, USA) in toluene (99.9%, Fisher Scientific, USA) 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® capillary column and a FID detector. Equilibrium constants for each isomerization step in reaction (1) were also calculated based on the ideal solution assumption following equation (2);

$$K_{i-j} = \frac{\alpha_j}{\alpha_i},$$

(2)

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% [7], with n-heptane (99%, Aldrich, USA) as a tracer. In addition, NaY (UOP LLC) as a potential adsorbent [8] was packed into the column with quantities varied from 15 to 75 mL of a 15 mL interval instead of the catalyst.
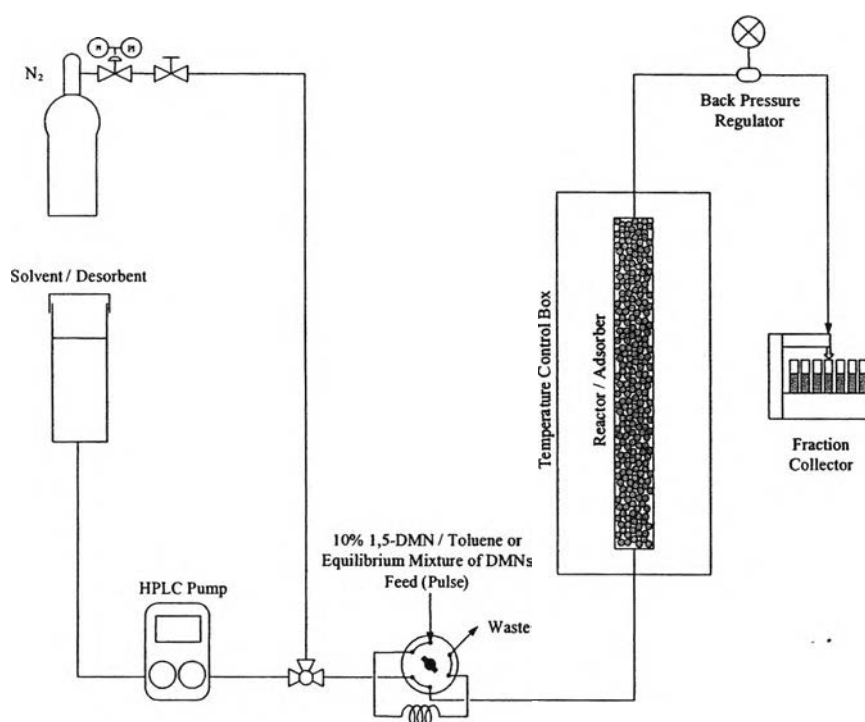
Figure 7.2 Experimental set up for isomerization, adsorption and reactive adsorption studies using the pulse test technique.

Then, the study on 2,6-DMN production by subsequently integrating the adsorption after the isomerization was performed using the experimental setup as shown in Fig. 7.3. Three mL of the catalyst was used with the appropriate liquid hour space velocity (LHSV), reaction temperature and absorbent amount as suggested by the previous experimental results. Firstly, 10 mL of 10 wt% 1,5-DMN in toluene as a feedstock was injected into the reactor and adsorber via the six-port valve number 1 to observe the DMNs profiles generated from the isomerization and subsequent separation over the catalyst and adsorbent, respectively. Afterward, 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 withdrawing 2,6-DMN was re-injected into the reactor and adsorber, simulating its utilization as a recycle stream to be further isomerized. Afterward, the 2,6-DMN lean stream collected at point D was re-injected to the system via the six-port valve number 1 and the experiment was conducted following the same procedure until the desired re-injection cycle has been reached. In addition, studying by re-injecting 10 mL of the feed at the six-port valve number 2 together with the 1,5- and 1,6-DMN rich stream (B), 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 to reach 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 (Fig. 7.2), 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.

7.4 Results and Discussion

7.4.1 Isomerization Study

The isomerization from 1,5- to 2,6-DMN was studied over a temperature range of 140 to 180°C using the pulse test technique. It should be noted that the employed H-beta zeolite only acts as a catalyst for the isomerization without providing any separation for the isomerized DMN products. By fixing the LHSV of the system at 15 h^{-1}, the concentration profiles of each isomerized DMN in the 2,6-triad after pulsing through the catalyst are illustrated in Fig. 7.4. It was found that all DMN profiles show the same behavior as those of the continuous test presented elsewhere [7]. Also, a slightly lower temperature to reach equilibrium is observed,

expected to be due to the dilution effect [7] during the pulse test. As a result, a temperature higher than 160°C is needed for the reaction to reach its equilibrium under the testing condition.
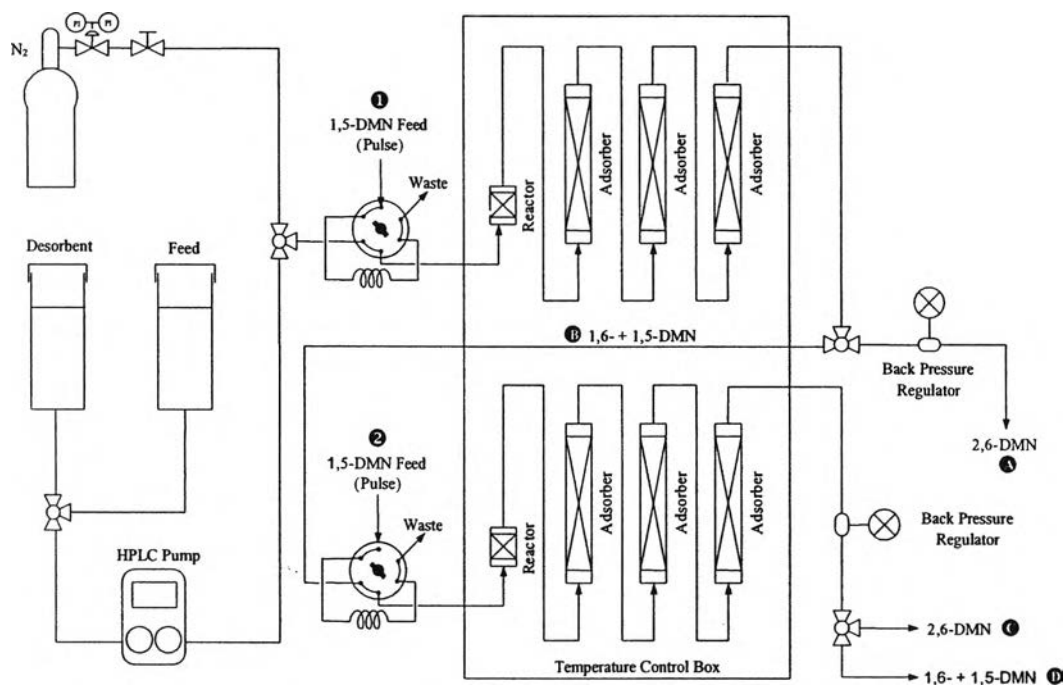

Figure 7.3 Experimental set up for study the production of 2,6-DMN by connecting the adsorbers subsequently to the reactor.
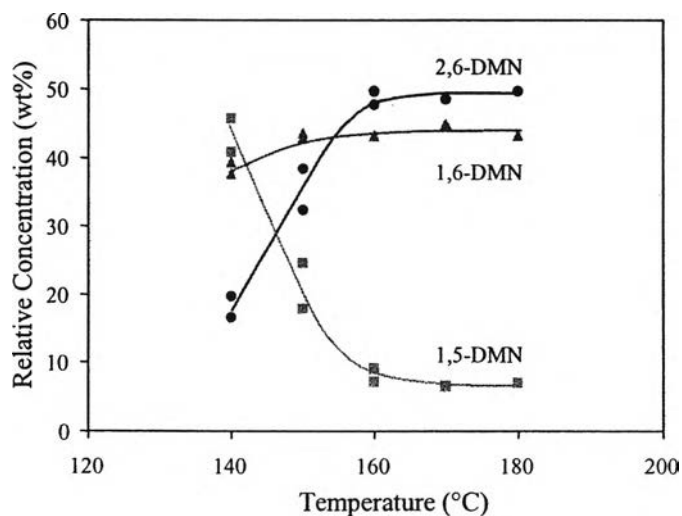
Figure 7.4 DMN distribution as a function of temperature from experimental pulse test of 10 wt% 1,5-DMN through the H-beta catalyst with 15 h^{-1} LHSV.

Fig. 7.5(a) shows the concentration profiles of the DMNs in the 2,6-triad as a function of the LHSV at 160°C. As expected, the increase in the flow rate lowers the amount of 2,6-DMN due to the lower contact time. The equilibrium constant of each step of the isomerization in equation (1) was then calculated using equation (2) and plotted as a function of the feed flow rate in Fig. 7.5(b). It was interestingly observed that the ratio between 1,6-DMN to 1,5-DMN is lower than that of the equilibrium, which is around 6.4, at the LHSV higher than 15 h^{-1} while the other ratio is not. This evidence indicates that the first step of 1,5- to 1,6-DMN isomerization needs more resident time on the catalyst than the second step of 1,6- to 2,6-DMN isomerization. Based on our findings on the isomerization thermodynamics in toluene media reported elsewhere [7], we believe that this phenomenon would be created by the differences in reaction kinetics of the two isomerization steps. For instance, the reaction rate of the first isomerization step from 1,5-DMN to 1,6-DMN would be lower than that of the subsequent isomerization from 1,6-DMN to 2,6-DMN, leading to a longer contact time requirement to reach equilibrium for the first one than the other. All in all, the system should be carried out with a LHSV lower than 15 h^{-1} to allow the isomerizations to reach their equilibrium under the testing condition.
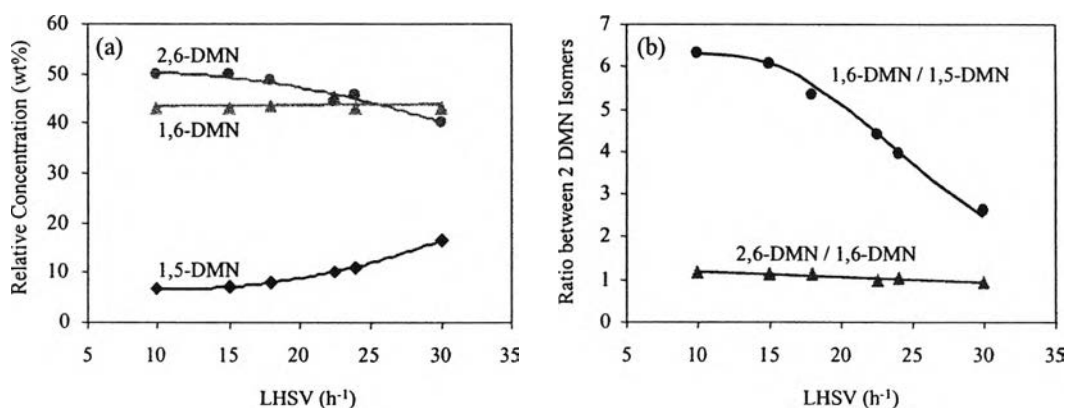

Figure 7.5 Variation with LHSV of (a) DMNs distribution and (b) calculated ratios between 2 DMN isomers from the pulse test of 10 wt% 1,5-DMN through H-beta catalyst at 160°C.

7.4.2 Adsorption Study

Purification of 2,6-DMN was investigated by means of adsorption over NaY with a fixed temperature and LHSV of the desorbent at 180°C and 1 h^{-1}, respectively. In this study, the amount of the adsorbent was varied to evaluate its appropriate quantity to be sufficient for the 2,6-DMN separation. Fig. 7.6 illustrates the pulse test results of the equilibrium isomeric mixture over different quantities of NaY. As expected, the increase in the adsorbent amount shows better 2,6-DMN separation from its isomeric mixture by providing a higher height equivalent to a theoretical plate (HETP). Also, the rejective system of 2,6-DMN is provided by NaY as observed and discussed elsewhere [8]. At least 45 mL of the adsorbent should be used to offer an adequate separation of 2,6-DMN from its equilibrium isomeric mixture.
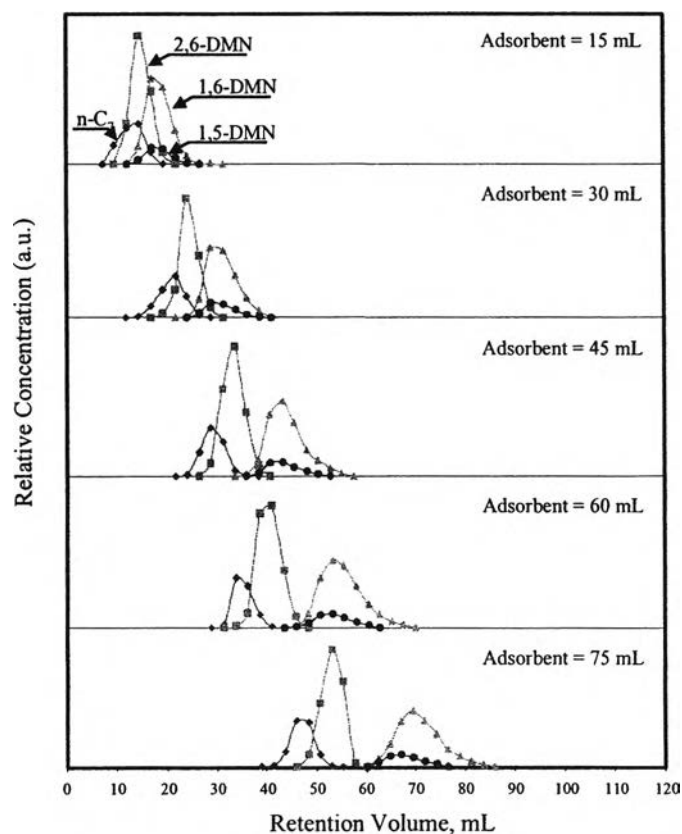

Figure 7.6 Pulse test results of the equilibrium 1,5-, 1,6- and 2,6-DMN mixture over different quantities of NaY at 180°C, 1 h^{-1} LHSV.

7.4.3 Study on the Production of 2,6-DMN by Subsequent Adsorption after Isomerization

The production of 2,6-DMN from the subsequent adsorption after isomerization was investigated by pulsing the feed (10 wt% 1,5-DMN in toluene) through the catalyst bed (3 mL of H-beta) before the adsorber (45 mL of NaY) under a fixed temperature of 160°C and a LHSV of 15 h^{-1} based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume). Fig. 7.7 shows the profiles of the isomerized DMNs eluted from the adsorber before and after re-injecting the 1,5- and 1,6-DMN rich stream into the reactor and adsorber. Fig. 7.7(a) suggests that the production of high purity 2,6-DMN is successfully accomplished using this technique as the high purity fractions of 2,6-DMN can be rejected as a raffinate under the testing condition. By removing the high purity 2,6-DMN from the isomerized products and re-injecting the stream containing less 2,6-DMN into the reactor and adsorber, the results shows further isomerization to equilibrium and separation to produce high purity 2,6-DMN as expected. Also, Fig. 7.7(c) and (d) exhibit that the re-injection can further yield the high purity 2,6-DMN as long as the concentration of 2,6-DMN in the re-injecting stream is lower than that of the equilibrium. This result potentially suggests that the simultaneous removal of the desired product from the isomerization stream, e.g. using the reactive adsorption technique, would enhance the overall yield of 2,6-DMN beyond the equilibrium limitation.

To evaluate the production of high purity 2,6-DMN under the more realistic system, an experiment on the re-injection of the feed together with the 1,5- and 1,6-DMN rich stream and a study by continuous feeding 30 mL of the feedstock instead of pulsing were carried out. It was found that the re-injection does not interfere both isomerization and adsorption of the system since the same equilibrium composition and elution profiles with only a difference in the DMNs quantities can still be achieved. In addition, the results from the study by continuous feeding the feedstock (Fig. 7.8) also show the potential to recover high purity 2,6-DMN from the isomerization product stream using such the system even in the continuous co-current operating mode. More details and discussion about the breakthrough profiles related to the 2,6-DMN purification can be found in elsewhere [8]. It is remarked that
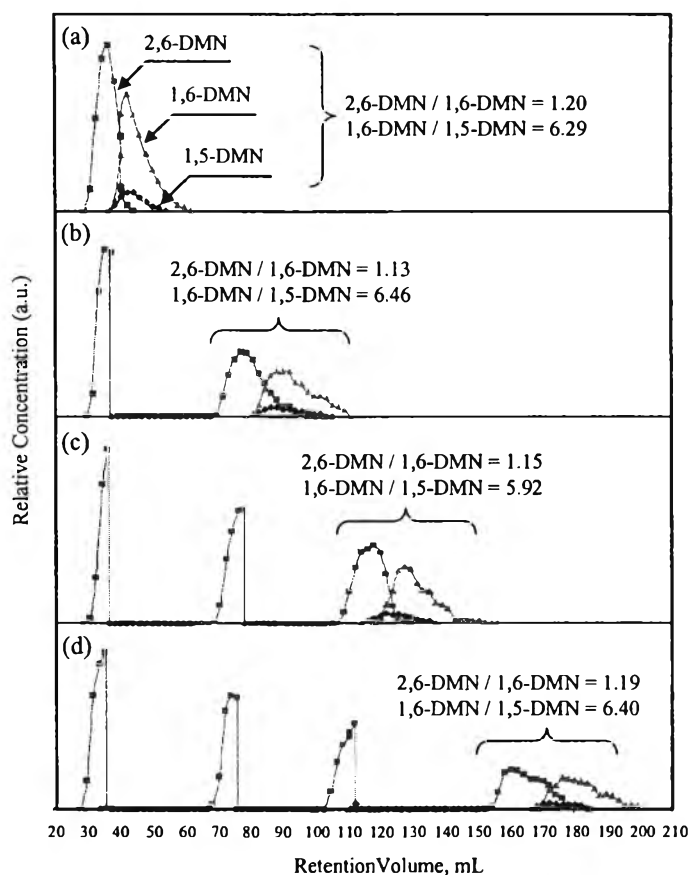
Figure 7.7 Pulse test results of 10 wt% 1,5-DMN through 45 mL of NaY after 3 mL of H-beta (a) before and after re-injecting the 1,5- and 1,6-DMN rich stream to the reactor and adsorber for (b) 1 cycle, (c) 2 cycles and (d) 3 cycles at 160°C, 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume).

the concentration of the feedstock in this study is not diluted as in the pulse test. So, the concentration effect is pronounced as expected, leading to a higher temperature required for the isomerization to reach equilibrium and an overlapping of the 1,5-DMN profile into the high purity zone of 2,6-DMN. A slight increase in the reaction temperature to 180°C can promote the isomerization to reach its equilibrium and overcome the 1,5-DMN impurity problem. As a result, the continuous production of high purity 2,6-DMN using the adsorption right after the isomerization seems to be better accomplished by continuous feeding the feedstock into the reactor, removing the high purity 2,6-DMN as a raffinate and recycling the extract stream containing the most 1,5- and 1,6-DMN to be fed together with the feedstock using a counter-

current simulated moving bed (SMB) adsorber right after the fixed bed isomerization unit as illustrated in Fig. 7.9. Even the proposed scheme is simple and general, it is totally different from the commercial process and expected to be accomplished with lower utility requirements. Better comparisons to the commercial process could be achieved by gathering more information from the pilot scale process.
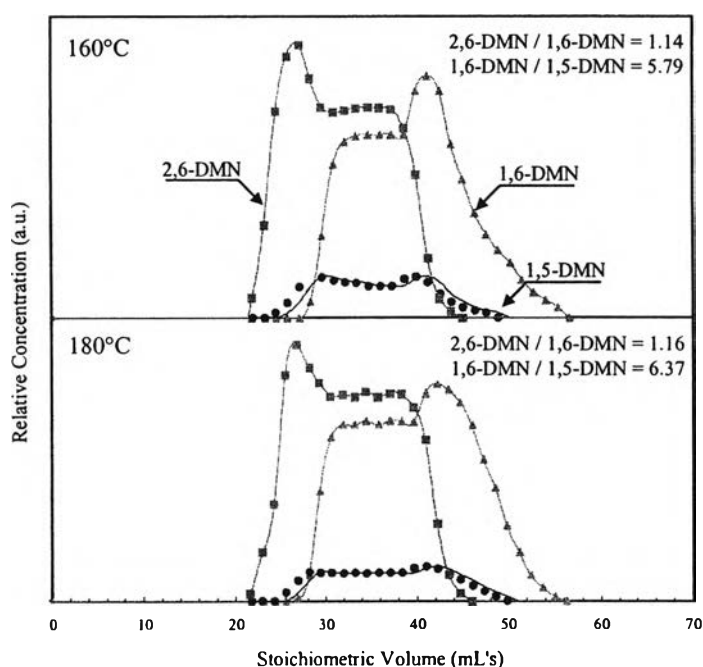

Figure 7.8 DMN concentration profiles from the continuously feeding a 30 mL of the feedstock to 45 mL of NaY after 3 mL of H-beta before the desorbent with 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume).

7.4.4 Study on the Production of 2,6-DMN Using the Reactive Adsorption Technique

The experimental pulse test over a physically mixed bed of 3:45 H-beta to NaY was conducted with a LHSV of 15 h^{-1} based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume) at 140 - 180°C. As exhibited in Fig. 7.10, the amounts of 1,5- and 1,6-DMN decrease as a function of temperature while that of 2,6-DMN increases due to the increase in the isomerization kinetics. By-products formation (1- and 2-methylnaphthalene and unknowns) was also

observed for the system conducted at 200°C. It was interestingly observed that the reactive adsorption based technique yields lower retention volumes of the 1,5- and 1,6-DMN profiles than those of the adsorption after isomerization system. This causes a reduction in the 2,6-DMN purity and lowers the quantity of high purity 2,6-DMN that can be produced using the system. Also, it seems that such the problem is more pronounced at high temperatures. Hence, carrying out the system at low temperatures is a better approach to produce high purity 2,6-DMN even with a lower conversion and yield of 1,5- and 2,6-DMN, respectively. Nevertheless, it was observed that the very low conversion of 1,5-DMN at 140°C as well as the very low diffusion rate through the adsorbent at this temperature [8] create a large broad profile of 1,5-DMN overlapping that of 2,6-DMN and lowering purity of the desired chemical. With increasing temperature, a slight separation of 2,6-DMN from its isomeric mixture can be achieved at 150°C, and being obstructed again at the higher temperatures. These results are due to the fact that the increase in the system temperature enhances the isomerization kinetics besides the rate of diffusion through the adsorbent; thus, the high purity 2,6-DMN fraction can be obtained from the system only when the reaction kinetics is not too fast to convert all the desorbed species from the adsorbent backwardly to the equilibrium. And, in this study, the temperature higher than 160°C can drive the isomerization to reach its equilibrium within the employed contact time (Fig. 7.4).
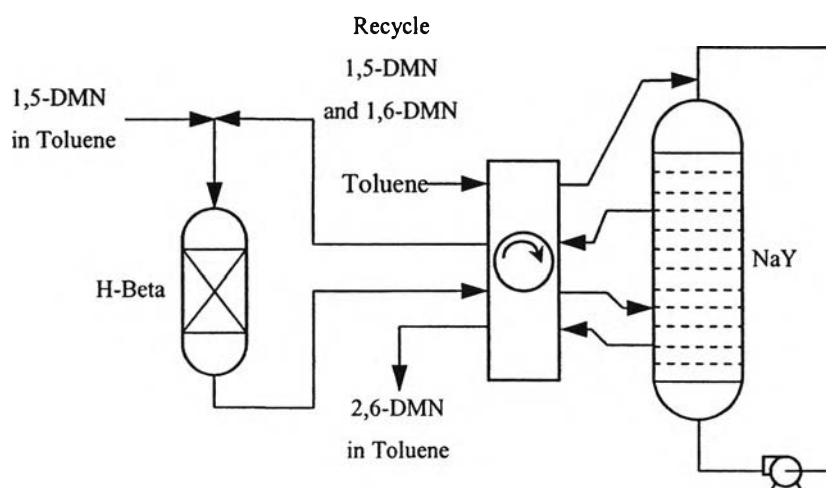

Figure 7.9 Proposed scheme for a continuous production of high purity 2,6-DMN by using adsorption after catalytic isomerization.
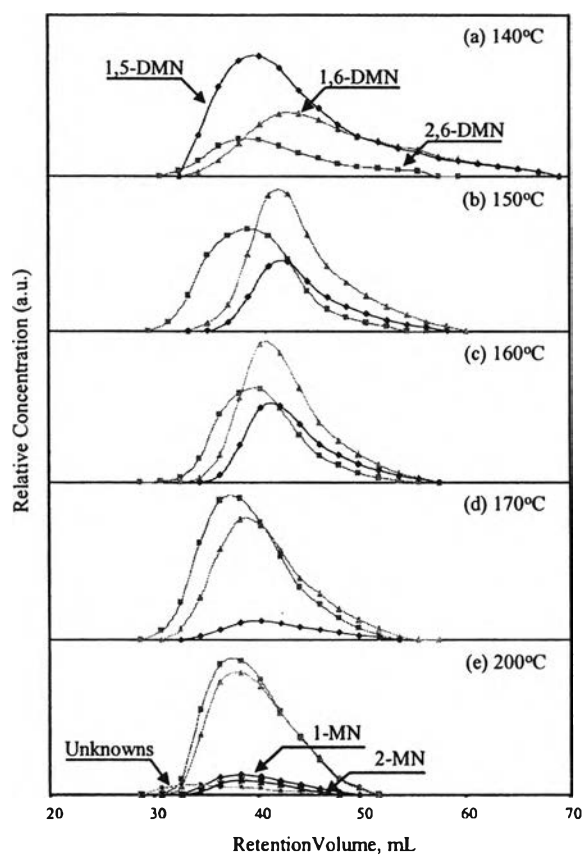
Figure 7.10 Pulse test results of 10 wt% 1,5-DMN through a physically mixed bed of H-Beta and NaY (3:45) with 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume) at (a) 140, (b) 150, (c) 160, (d) 170 and (e) 200°C.

The relative concentration of the DMN species in the 2,6-triad of the effluent was determined and plotted as a function of temperature with the calculated DMN ratios in Fig. 7.11. The results confirm that the isomerizations are at their equilibrium at temperatures higher than 170°C. Interestingly, it was observed that the calculated DMN ratios of the reactive adsorption system at 160°C are significant lower than those of the reaction study, which are at the equilibrium. This result suggests that the isomerization would be backwardly driven from 2,6- to 1,6- and 1,5-DMN. This is probably due to the slightly lower in the catalyst activity than that at 170°C that would preferentially isomerize the rejected species (2,6-DMN) to the equilibrium than the adsorbed species (1,5- and 1,6-DMN). In such the case,
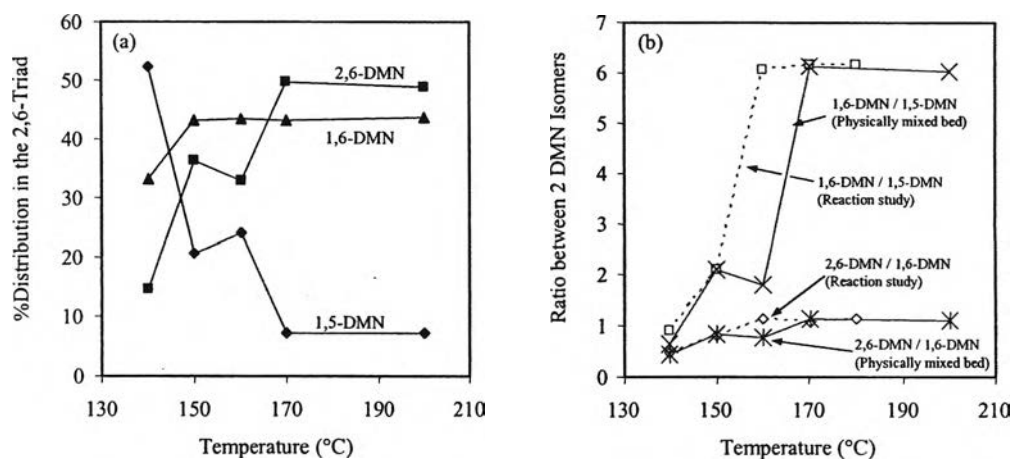
Figure 7.11 Variation with temperature of (a) DMN distribution in the 2,6-triad and (b) calculated ratio between 2 DMN isomers from experimental pulse test of 10 wt% 1,5-DMN through a physically mixed bed of H-Beta and NaY (3:45) with 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume).

2,6-DMN that tends to be rejected from the adsorbent would be backwardly converted to equilibrium over the catalyst the most, while the other strongly adsorbed species would be converted in the lower extent. Thus, the DMN ratios are below those of the equilibrium. As the temperature being reduced below 160°C, the isomerization seems not be able to reach its equilibrium due to an insufficient in either the reaction kinetics or mass transfer of the system as discussed elsewhere [7]. Hence, the catalyst cannot convert all the desorbed species from the adsorbent to equilibrium, leading to a slight separation of 2,6-DMN, substantiating our beforehand discussion. However, lowering the temperature also lowers the conversion of 1,5-DMN that can obstruct the separation of 2,6-DMN as well.

In order to validate the hypothesis that the isomerization is backwardly shifted at 160°C, the reactive adsorption experiments were also conducted at a higher and lower feed flow rate. As exhibited in Fig. 7.12, it seems that the increase in the LHSV results in a slightly better 2,6-DMN separation compensated with the lower conversion of 1,5-DMN due to the lower contact time. It should be noted that the separation at the higher flow rate is not obviously improved

as in the case of reducing the temperature because the separation itself is normally obstructed under such the high flow. On the other hand, reduction of the feed flow rate provides more time for the catalyst to produce 2,6-DMN, which also suppresses its separation from the isomerized products as previously observed in the case of increasing temperature. Fig. 7.13 exhibits the relative concentration of the DMN species in the 2,6-triad and their ratios as a function of the LHSV. As expected, the decrease in the LHSV results in the higher 2,6-DMN production and the closer the calculated DMN ratios to those of the equilibrium.

Reducing the catalyst to adsorbent ratio can also enhance the yield and the separation of 2,6-DMN as demonstrated in Fig. 7.14 and 7.15. This result substantiates the previous hypothesis about the backward shift of the reaction equilibrium at the testing temperature. It is also noted that the slight increase in the DMN ratios does not indicate the inferior role of the catalyst amount compared to that of the feed flow rate because the decrement of the catalyst amount creates the increase in the LHSV based on the catalyst volume in the higher magnitude.

All in all, the results indicate a narrower possible operating window to produce high purity 2,6-DMN with the reactive adsorption technique using a physically mixed bed of H-beta and NaY than the conducting adsorption right after the isomerization. The system should be carried out in the non-equilibrium region at low enough temperatures to provide a sufficient conversion of 1,5-DMN, e.g. at between 140 – 150°C, using counter-current SMB reactor as illustrated in Fig. 7.16. Even though this restricted operating conditions lead this process to yield a lower quantity of high purity 2,6-DMN than the first integration approach, a better energy management from this simple unit operation would give another benefit to be considered. This suggests a possibility of the reactive adsorption process as a potential competitive to both the commercial and the adsorption after the isomerization processes.
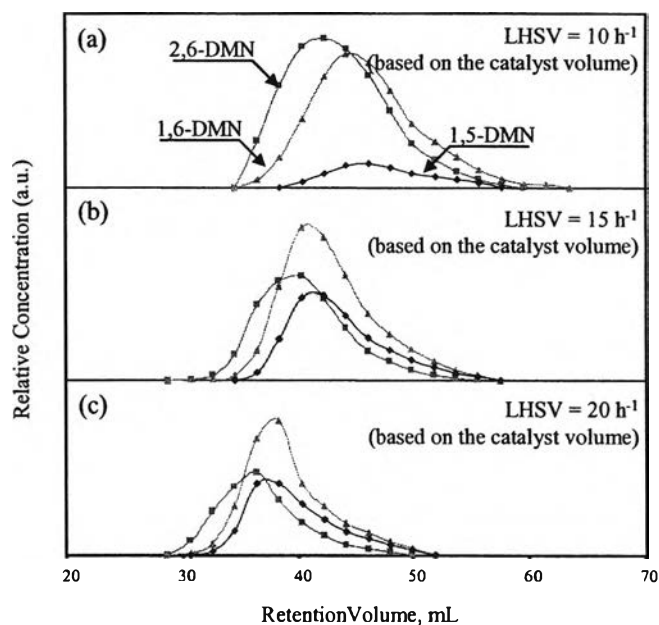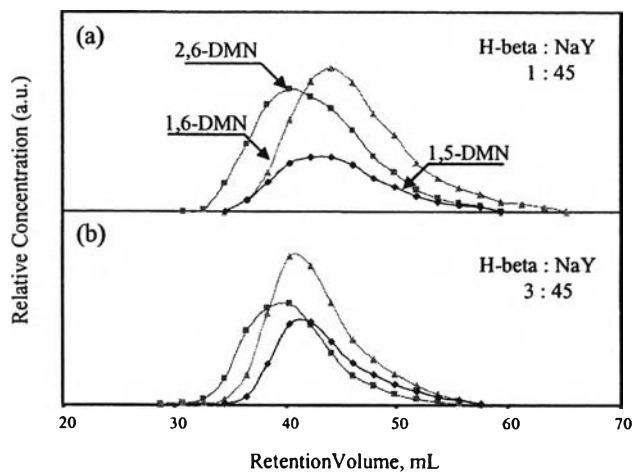
Figure 7.12 Pulse test results of 10 wt% 1,5-DMN through a physically mixed bed of H-Beta and NaY (3:45) at 160°C with LHSV of (a) 10, (b) 15 and (c) 30 h⁻¹ based on the catalyst volume.
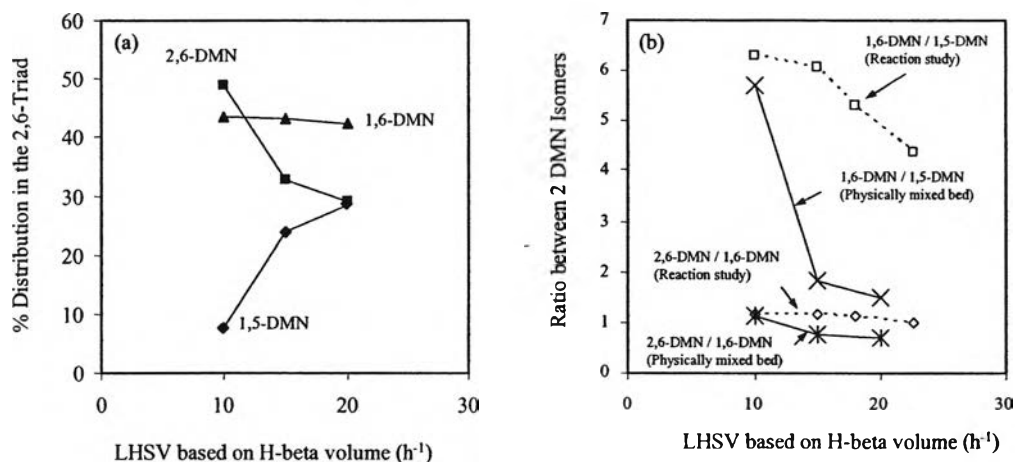

Figure 7.13 Variation with LHSV of (a) DMN distribution in the 2,6-triad and (b) calculated ratio between 2 DMN isomers from experimental pulse test of 10 wt% 1,5-DMN through a physically mixed bed of H-Beta and NaY (3:45) at 160°C.

Figure 7.14 Pulse test results of 10 wt% 1,5-DMN through a physically mixed bed of H-Beta and NaY with a ratio of (a) 1:45 and (b) 3:45 at 160°C, 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume).
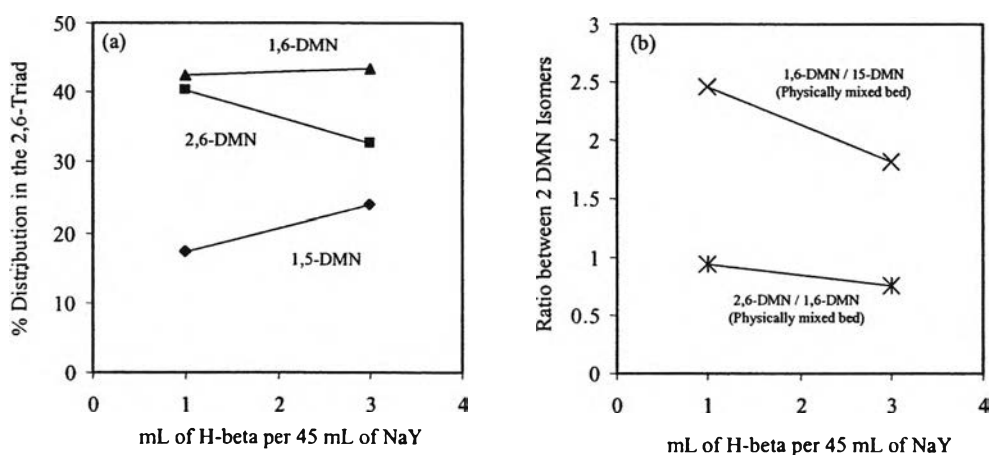
Figure 7.15 Variation with H-beta : NaY ratio of (a) DMN distribution in the 2,6-triad and (b) calculated ratio between 2 DMN isomers from experimental pulse test of 10 wt% 1,5-DMN at 160°C, 15 h^{-1} LHSV based on the catalyst volume (corresponding to 1 h^{-1} based on the adsorbent volume).
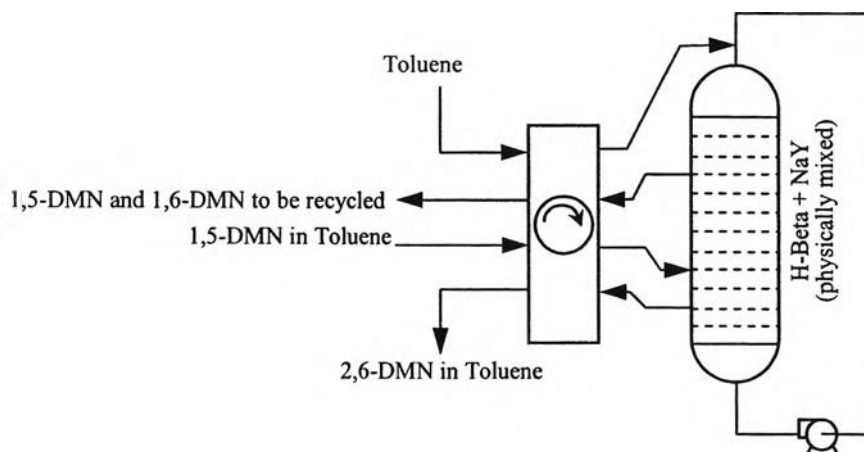
Figure 7.16 Proposed scheme for a continuous production of high purity 2,6-DMN by SMB reactor based the reactive adsorption technique.

7.5 Conclusions

The production of high purity 2,6-DMN using the integration of the isomerization in a solvent media to the adsorptive purification was investigated in two different approaches. The results show a high potential for high purity 2,6-DMN production by subsequent connecting the adsorption unit after the isomerization with the selected adsorbent, catalyst and desorbent. However, only a narrow possible operating window was revealed for the reactive adsorption based production. This is due to the very fast reaction kinetics of the catalyst at high temperatures that entails the reduction in either the 2,6-DMN separation by driving the reaction reaching its equilibrium or the 2,6-DMN yield by the backward isomerization from 2,6- to 1,6- and 1,5-DMN. As a result, operating the system below the equilibrium of the isomerization at appropriate temperatures is only a possible approach to produce high purity 2,6-DMN using the reactive adsorption technique.

7.6 Acknowledgements

7.7 Nomenclature

K_{i-j} thermodynamic equilibrium constant of reactant i to product j isomerization

$K_{1,5-1,6}$ thermodynamic equilibrium constant of 1,5-DMN to 1,6-DMN isomerization

$K_{1,6-2,6}$ thermodynamic equilibrium constant of 1,6-DMN to 2,6-DMN isomerization

Subscripts

i of reactant i

j of product j

7.8 References

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