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Influences of solvents on the production of high purity 2,6-dimethylnaphthalene via catalytic isomerization and adsorptive separation

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Abstract

Influences of seven solvents – benzene, toluene, ethylbenzene (EB), *p*-diethylbenzene (*p*DEB), *o*-xylene, *m*-xylene, and *p*-xylene – on the production of high purity 2,6-dimethylnaphthalene (DMN) via catalytic isomerization and adsorptive separation of the 2,6-triad DMNs were investigated. The solvents act as a reaction media for the isomerization and a desorbent for the adsorption. From the catalytic testing in a batch reactor over a H-beta catalyst and the adsorption using a pulse test technique over Na-faujasite adsorbents, the results indicate that the solvent characteristics, e.g. dipole moment, relative π-electron basicity, play very important roles on both processes. And, the best catalytic isomerization and adsorption system can be demonstrated if an appropriate solvent is used. Among the employed solvents, appropriate solvents for either the isomerization or adsorption were identified in this study. However, only toluene shows a possibility for being used to produce high purity 2,6-DMN via the combination of the isomerization and adsorption technique.

Keywords: Dimethylnaphthalene; Isomerization; Adsorption; Desorbent

1. Introduction

2,6-Dimethylnaphthalene (DMN), a precursor to polyethylene naphthalate (PEN), is known as one of the major obstructions to produce PEN in a comparable price to those of other polyesters [1–7]. This is because of the large-scale production of 2,6-DMN needs a lot of energy and complicated systems to obtain acceptable throughput and purities. For example, most of many patented processes fail to produce 2,6-DMN with a high yield at low temperatures or without any side products formation [5–7]. Particularly when other DMN isomers are formed, the isolation of 2,6-DMN is very difficult. On one hand, the very close in boiling points of DMN isomers makes the use of conventional distillation methods not practical for an industrial requirement of 2,6-DMN purity [1,6,7]. On the other hand, the very high wettability of 2,6-DMN crystal and its potential to form a eutectic mixture with other isomers lead to the difficulty in using crystallization to purify 2,6-DMN even it possesses a significant different freezing temperature from the others [6,7].

To alleviate such the problems, many attempts have been made to find the most selective and effective approach to produce 2,6-DMN with both lower energy utilization and side products formation. The largest commercialized process licensed by BP Amoco is one of the successful examples in the economic point of view. The process employs a complex liquid phase reaction-in-series with a use of toluene and butadiene as reactants. More importantly, the use of H-beta zeolite for the final 2,6-triad isomerization of the process, Eq. (1), is claimed to substantially suppress the DMN disproportionation and the isomerization across the triad, which is inevitably encountered when using other types of acidic or bi-functional catalysts [5–9]. As a result, such the separation difficulties can be significantly lowered since only the separation of 2,6-DMN from 1,5- and 1,6-isomers is required. Nevertheless, a rather low 2,6-DMN throughput as well as a high utility consumption are still the

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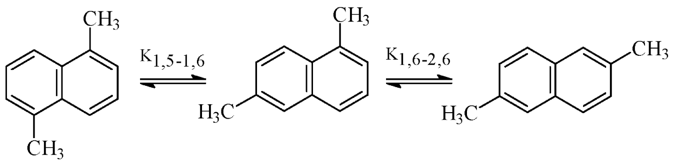
current major drawbacks of the process [1]:



(1)

For the 2,6-triad isomerization, its high endothermicity and thermodynamic control result in a limit to which only 48 wt.% of 2,6-DMN can be produced at high equilibrium temperature [1–3]. This limitation is recently suggested by Kraikul et al. [4] to be better confronted by conducting such the isomerization in toluene media. They discover that the use of toluene would provide advantages on the improvement of the system mass transfer and modification of the isomerization thermodynamics besides facilitation the reaction for continuous operation in the liquid phase. Consequently, the maximum yield of 2,6-DMN at the high temperature can be accomplished at significant lower temperatures and also without any side reaction.

In addition, Kraikul et al. [4] also reported the success of using an adsorption technique to purify 2,6-DMN from its isomeric mixture instead of using the energy intensive freeze crystallization as employed in the commercial process. With the use of toluene and some appropriate ion-exchanged faujasite zeolites (e.g. KX, CaX, LiY, NaY, KY, RbY, SrY, and BaY) as a desorbent and adsorbent, respectively, high purity 2,6-DMN fractions can be effectively recovered with purity close to 100 wt.% [10]. Based on their discovery, they proposed a new approach to produce high purity 2,6-DMN by integrating the catalytic isomerization to the adsorptive purification with the use of toluene as a media [11]. Therefore, high purity 2,6-DMN could be produced with a lower cost.

It seems that the use of solvent plays very important roles in the high purity 2,6-DMN production. And, the 2,6-DMN isomerization and separation could be significantly improved if an appropriate solvent is employed. Until now, no attention has been paid for this issue. Thus, in this work, seven solvents – benzene, toluene, ethylbenzene (EB), *p*-diethylbenzene (*p*DEB), *o*-xylene, *m*-xylene, and *p*-xylene – were studied for their influences on the catalytic isomerization of 1,5-DMN to 2,6-DMN over H-beta catalyst. The adsorption over selected faujasite adsorbents (NaX and NaY) were investigated and discussed.

2. Experimental

2.1. Catalytic isomerization experiments

Catalytic isomerization of 1,5-DMN along the 2,6-triad was batch-wisely conducted using an autoclave reactor. The reactant was prepared by dissolving 10 wt.% of a solid feedstock, 1,5-DMN (96% purity, Aldrich), into one of the employed solvents, which were benzene (99% purity, Fisher Scientific), toluene (99.9%, Fisher Scientific), ethylbenzene (EB) (99.8% purity, Aldrich), *p*-diethylbenzene (*p*DEB) (98% purity, Acros), *o*-xylene (99% purity, Sigma–Aldrich), *m*-xylene (99% purity, Sigma–Aldrich) and *p*-xylene (99% purity, Aldrich). Table 1 lists the employed solvents with their dipole moments, molecular sizes and relative basicity to benzene. All solvents were treated using silica gel prior to experiments, except benzene that was used as received. Then, a 20–40 mesh H-beta zeolite (24 SiO_2/Al_2O_3, 25% alumina binder, UOP LLC) was poured into the autoclave with a fixed amount of 5 wt.% with respect to the feed amount. After that, the autoclave was heated to desired temperatures and held for 2 h with periodical shaking. 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.

Table 1
Solvents with their dipole moments, molecular sizes and relative basicity to benzene

Solvent	Dipole moment (D)[a]	Kinetic diameter (A°)	Relative basicity to benzene[g,h]
Benzene	0	5.85[b]	1.0
Toluene	0.36	5.85[c]	1.5
Ethylbenzene	0.59	6[d]	1.5
p-Diethylbenzene	0	7[e]	1.55
o-Xylene	0.62	6.8[f]	1.8
m-Xylene	0.33	6.8[f]	2.0
p-Xylene	0	5.85[b]	1.6

(a) from [12] values for 1,5-, 1,6- and 2,6-DMN are 0.07, 0.32 and 0.14 D, respectively. (b–f) from [13–17]. Values for 1,5-, 1,6- and 2,6-DMN are 7.7°, 7.7° and 7.2 A°, respectively. (g and h) from [18,19].

2.2. Dynamic adsorption experiments

The pulse test technique was employed to study the influences of using such the solvents as desorbents to purify 2,6-DMN by means of adsorption. Firstly, the equilibrium mixture of 2,6-triad DMNs consisting of 8 wt.% 1,5-DMN, 43 wt.% 1,6-DMN and 49 wt.% 2,6-DMN was synthesized following the condition presented elsewhere [4]. Then, 10 wt.% of the DMNs equilibrium mixture was prepared using a desired desorbent and used as a feed. Five weight percent of *n*-nonane (99% purity, Aldrich) was also added into the feed as a tracer. Na-faujusite (FAU) zeolites obtained from UOP LLC (USA) were dried at 350 °C for 1 h before using as adsorbents.

Experimental pulse testing was conducted by packing the adsorbent into a 70 mL stainless steel adsorber before subsequently filling with a selected desorbent of a 1.2 mL/min fixed flow rate, equivalent to 1 h^{-1} LHSV. After the system reached a desired temperature and pressure of 180 °C and 500 psi, respectively, 5 mL of a feed mixture was pulsed into the adsorber. The effluent was collected using a fraction collector for quantitative analysis using a GC equipped with an FID detector and the ULBON® PLC capillary column. The elution profile was then plotted between the composition and the retention volume of the effluent. By comparing the retention volume of the tracer to those of the DMNs, the net retention volumes (NRVs) were obtained. Relative adsorption selectivity of the species was then calculated using the ratio between the NRVs of the two interesting species.