추출결정화를 이용한 2,6-, 2,7-DMN 혼합물로부터 2,6-DMN의 분리

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Separation of 2,6-DMN in 2,6- and 2,7-DMN Mixtures by Extractive Crystallization

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INTRODUCTION

2,6-Dimethylnaphthalene (2,6-DMN) in naphtha cracking raffinates is an important material because it is the starting material for the manufacture of polyethylene naphthalate (PEN) and liquid crystal polymer (LCP). PEN has especially received much attention because of its higher performance properties in respect of heat resistance, elasticity, chemical stability, and gas barrier than polyethylene terephthalate (PET). Such higher performance properties make it possible to be used in applications such as special films, fibers, reaction containers, and packings. Therefore, with expansion of PEN applications, the need for 2,6-DMN will increase. To enhance the quality of PEN, 2,6-DMN must be essentially purified. The naphtha cracking raffinate consists of close-boiling hydrocarbons with dimethylnaphthalene (DMN) isomers. The conventional processes [1] as a distillation and adsorption for separation of 2,6-DMN from the raffinates have a limitation at the purity and yield of products because of close boiling point. Therefore, Crystallization [2] was one possibility to apply to purification of 2,6-DMN from raffinates. Melt crystallization technique was highly purified from eutectic system but it cannot above eutectic point. Therefore, extractive crystallization can be used in purification. A third component usually a liquid called the extract is added to the two components to modify the solid-liquid phase behavior. This extraneous agent does not form a solid phase at any point in the process. This process is known by the name extractive crystallization [3]. Findly et al. [4] describe in detail an extractive crystallization process in which p-xylene and m-xylene are completely separated from each other by using n-heptane as the extractive solvent. A detailed review of successful separation by extractive crystallization has been given by Chivate and Shah [5] and Diksht and Chivate [6]. Many organic mixtures with its isomer were separated by extractive crystallization. However, the separation of 2,6-DMN from raffinates by extractive crystallization has not yet been successfully reported.

Separation and purification of 2,6-DMN from naphtha cracking raffinates be carried out in the previous work [7]. However, the product obtained in separation of 2,6-DMN from naphtha cracking raffinates contains 2,7-DMN as a major impurity. Therefore, this work was to explore the separation of 2,6-DMN from 2,6- and 2,7-DMN mixtures by extractive crystallization.

EXPERIMENTAL

The mixtures were prepared by mass using a Metter AG 204 balance with an accuracy of ±0.0001 g. The estimated accuracy in the mass fraction is less than $\pm 2 \times 10^{-4}$. Reagent-grade 2,6-DMN and 2,7-DMN (Aldrich Chemical Co.) were used. Gas chromatographic analysis indicated that their purities were more than 99 %.

The experimental crystallizer [8] was made of Pyrex glass with a jacketed vessel with a total volume of 200 mL. It was equipped with an agitator, marine propeller type with a 40 mm diameter at a set speed of 300 rpm. The temperatures of the inside crystallizer and the thermostat bath were recorded by digital temperature recorder. The temperature of the crystallizer was controlled by PID temperature controller with an error range of ±0.05 K. The mixtures of crude weighed accurately were prepared in the crystallizer, and the mixtures were agitated until the crude was dissolved. The mixtures of crude and extract weighed accurately were prepared in the crystallizer, and the mixtures were heated by circulating thermostatic medium until the crude was dissolved in extract. Methanol as a cooling medium was thermostated and controlled by a thermoelectric Eurotherm 808 PID controller with 0.1 K accuracy. The cooling rate of crystallization was set constantly in the range from 0.01 K/min to 10 K/min. The crystals are separated by vacuum filtration from residual solution. An image analysis (Image-Pro Plus) system installed with a CCD color camera (TOSHIBA) was used to measure crystal size and crystal morphology. The products were analyzed by FID DONAM GC 6200 gas chromatography (GC) equipped with capillary columns; Shinwa, GC-8A capillary column ULBON HR-1.

RESULTS AND DISCUSSION

The product obtain in the separation process of 2,6-DMN from naphtha cracking raffinates contains 2,7-DMN as an impurity. Therefore, it is required that separation of 2,6- and 2,7-DMNs contained in final product must be considered. The melting points of 2,6- and 2,7-DMNs are 383 and 371 K, respectively. These two components form a simple eutectic mixture as shown in Fig. 1.
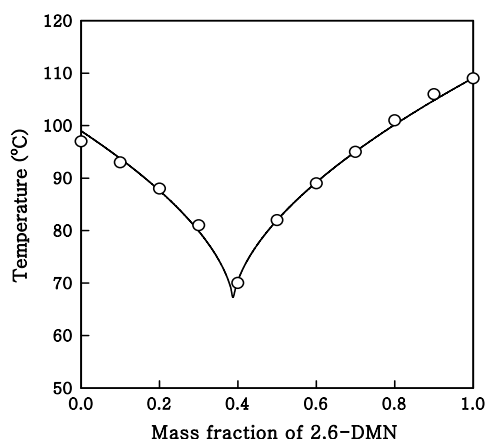

Fig. 1. Binary phase equilibrium diagram
of 2,6-DMN and 2,7-DMN.

The present research investigates the efficiency of novel crystallization techniques for the

separation of 2,6- and 2,7-DMNs from their mixtures. The end product in the separation of 2,6-DMN from raffinates will contain an isomeric mixture of mainly 2,6- and 2,7-DMNs and these cannot be separated by conventional separation techniques. A ternary diagram of the solid-liquid phase behavior for a three-component system with simple eutectic is shown in Fig. 2. Components A (2,6-DMN) and B (2,7-DMN) are the two components to be separated and the feed composition is represented in the phase diagram by the point F. The binary eutectic points are represented by E_1, E_2, and E_3 and the ternary eutectic point is represented by T. We recommend that experimental verification of the solid-liquid phase diagram predicted by models be an integral step in flowsheet development. The appropriate flowsheet structure for this phase diagram is shown in Fig. 3.
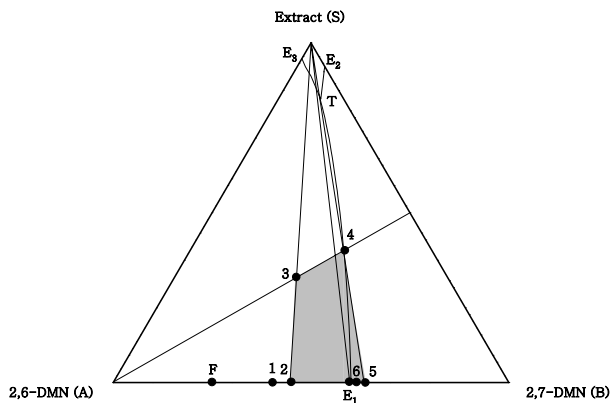

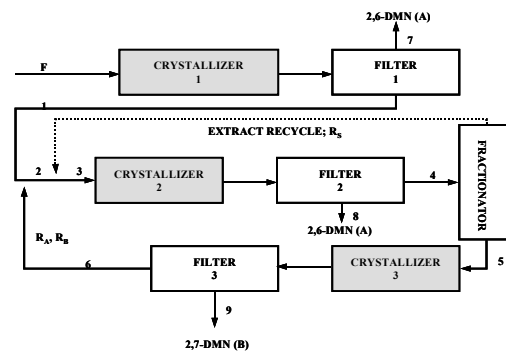Fig. 2. Solid-liquid phase diagram for 2,6-DMN, 2,7-DMN and extract system.

Fig. 3. Process flowsheet for separating DMN isomers.

The compositions of the liquid phase in various streams of the process are indicated by numbers in the flowsheet ad well as in the phase diagram. The liquid phase compositions in the process at various points in the flowsheet lie within the shaded area 2345 in Fig. 2. Three crystallizers and three filters are needed for this separation scheme. The feed stream is represented by point F in the phase diagram, Fig. 3, and is fed to the first crystallizer, where the temperature is maintained at TC_1. A is crystallized from the feed and is separated from the mother liquor in the first filter. The composition of the mother liquor from the crystallizer moves down to point 1 in the phase diagram. The recycled A and B mixtures from the third crystallizer with composition represented by 6 is added to this stream. The composition of the mixed stream is represented by point 2 in the phase diagram. The recycled S (extract) from the extract recovery fractionator is added to this new stream. The mixed stream with composition represented by point 3 is fed to the second crystallizer. The temperature of the second crystallizer is maintained at TC_2, and more A is crystallized from the solution. The mother liquor is fed to the extract recovery fractionator, where the extract is separated and recycled to the second crystallizer feed. The fractionator bottom with composition 5 is fed to the third crystallizer. The third crystallizer temperature is maintained at TC_3 and B is crystallized from the solution. The A crystals are separated from the mother liquor in filter 3. The mother liquor, whose composition is represented by point 6, is recycled to the second crystallizer feed stream. As will be seen in the design equations to be discussed, the amounts of components A and B crystallized in the three crystallizers can be exactly matched to the amounts in the feed stream by manipulating the recycle flow rates of the extract, component

A, and component B, and the three crystallizer temperatures. The material balance is tabulated in Table 1. From the material balance it can be seen that extractive crystallization produces high purity products of A and B. As can be seen from the material balance, three product streams are produced. The mother liquor composition moves further down to point 4 in the phase diagram. The crystals are separated from the mother liquor in filter 2. The extractive crystallization has the advantage of producing two high purity products from the original A, B binary system which forms a eutectic. This indicates that higher costs of extractive crystallization must be justified on the basis of minimizing the amount of feedstock required, the recovery of two products which have a high price, or the recovery of products which cannot be separated by any other conventional means.

Table 1. Extractive crystallization material balance (basis: 100 g/min)

	Stream flow rates (g/min)									
	F	1	2	3	4	5	6	7	8	9
2,6-DMN	75.0	32.7	33.1	33.1	0.1	0.1	0.4	42.3	33.0	0.1
2,7-DMN	25.0	24.1	24.1	24.1	24.8	24.8		2.2	0.2	24.8
Extract				198.0	198.0	2.0	2.0			
Total	100.0	56.8	57.2	255.2	222.9	26.8	2.4	44.5	33.2	24.9
2,6-DMN(wt%)	75.0	57.6	57.9	13.0	0.1	0.4	16.7	95.0	99.5	0.4

CONCLUSIONS

The separation and purification of 2,6-DMN from 2,6- and 2,7-DMN mixtures were studied by extractive crystallization. The degrees of purification achieved for purifying 2,6-DMN by extractive crystallization using various extracts were explored. The high separation efficiencies achieved in the laboratory-scale experiments illustrates the high potential for application of extractive crystallization processes in purification of 2,6-DMN of commercial interest. As the experimental results, yield and purity of product in extractive crystallization operations were considered and process for purification of 2,6-DMN was optimized. This method will be probably one of the possible separation methods for not only the DMN isomers but also other structural isomeric mixtures in the industrial separation process. Further experiments and study on the separation mechanism at extractive crystallization, and the bench and pilot tests are needed. An effective separation process of close-boiling isomers will be designed based on the more detailed results.

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