

결정화 조작에 의한 Dimethylnaphthalene 이성체 혼합물 중의 2,6-dimethylnaphthalene의 분리

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Separation of 2,6-dimethylnaphthalene in Dimethylnaphthalene Isomers Mixture by Crystallization Operation

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접촉분해 가솔린 제조공정의 부산물의 하나인 접촉분해경유(LCO)는 많은 유용 방향족 성분을 함유하고 있다. 그 중에서도 특히 2,6-dimethylnaphthalene (2,6-DMN)은 PEN 수지, 고분자 액정 등의 기초 원료로서 주목된다. 지금까지 증류에 혼합되어 연료로서만 사용되고 있는 LCO로부터 2,6-DMN 등과 같은 유용 방향족 탄화수소를 분리, 정제하는 것이 가능하게 되면 자원의 유용이용이라는 관점에서 그 의미는 매우 크다. 본 연구는 melt crystallization (MC)과 solute crystallization (SC)의 조합에 의해 2,6-DMN의 고순도 정제를 검토했다. MC와 SC의 원료로서는 증류-추출 조합에 의해 LCO로부터 회수한 DMN 이성체 혼합물(2,6-DMN의 농도: 10.43%)과 MC로부터 회수한 결정을 각각 사용했다. SC의 용매는 메탄올과 아세톤 혼합물(60 : 40 wt%)을 사용했다. MC-SC의 조합에 의해 99.5%의 2,6-DMN 결정을 회수할 수 있었다. MC-SC는 DMN 이성체 혼합물에 함유된 2,6-DMN의 고순도 정제에 매우 유용한 조합의 하나임을 확인했다.

Light cycle oil (LCO), one of the by-products of the catalytic cracking gasoline manufacturing process, contains a lot of valuable aromatics. In particular, 2,6-dimethylnaphthalene (2,6-DMN) contained in LCO has been becoming important as the basic material of polyethylene naphthalate plastic and liquid crystal polymer, etc. If it were possible to separate and purify the valuable aromatic hydrocarbons (such as 2,6-DMN) from LCO, which have only been used as fuel mixed with heavy oil, it would be very meaningful in terms of the efficient use of resources. We investigated the high-purity purification of 2,6-DMN by the combined method of melt crystallization (MC) and solute crystallization (SC). The enriched DMN isomer mixtures (concentration of 2,6-DMN : 10.43%) recovered from LCO by distillation-extraction combination and the crystal recovered by MC used as raw materials of MC and SC, respectively. The solvent of SC used was a mixture of methanol and acetone (60 : 40 wt%). The crystal of 2,6-DMN with a high-purity of 99.5% was recovered by MC-SC combination. We confirmed that the MC-SC combination was one of the very useful combinations for the high-purity purification of 2,6-DMN contained in the enriched DMN isomer mixtures.

Keywords: light cycle oil, 2,6-dimethylnaphthalene, high-purity purification, melt crystallization - solute crystallization combination, engineering plastic

1. Introduction

High performance polymers have been increasingly used as alternative materials of metal and conventional plastic in industrial material fields,

such as automobile, electron, electricity, and precision machine. The high performance polymer materials, in particular of which representative materials are the engineering plastic, are relatively expensive compared to conventional-plastic, but have excellent properties in terms of dynamic characteristics, heat resistance, and chemical characteristics. Terephthalic acid like aromatic dicarboxylic acid, has been widely used in producing various polyesters (which are the main compounds of the polymers), but 2,6-naphthalene dicarboxylic acid (2,6-NDA), which is produced by the oxidation reaction of 2,6-dimethyl naphthalene (2,6-DMN), is recently getting the spotlight as the raw material to produce the high

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Table 1. Physical Properties of DMN Isomers

Component	b.p.* (°C)	m.p.** (°C)	c.d.*** (Å)
2,6-DMN	262.0	112.0	5.80
2,7-DMN	262.3	98.0	5.80
1,7-DMN	262.7	-14.0	6.55
1,3-DMN	264.8	-4.2	6.55
1,6-DMN	265.7	-16.0	6.20
1,4-DMN	265.0	6.0	7.20
2,3-DMN	269.2	105.0	5.80
1,5-DMN	269.1	82.0	6.20
1,2-DMN	271.4	-3.5	6.20
1,8-DMN	270.0	65.0	6.55

* : boiling point, ** : melting point, *** : critical molecule dimension.

performance polymers because it is excellent in terms of structural stiffness and planarity. 2,6-NDA is not only used as the monomer to produce polyethylene naphthalate (PEN), the general heat resistance polyester surpassing polyethylene terephthalate (PET), via the esterification with ethylene glycol and subsequently polycondensation reaction, but also as the monomer of various copolyarylates, namely the aromatic polyesters. The polymers are expected to be widely used to produce sheet, film, and textile, with a heat resistance over 250 °C and good mechanical properties. Also they can form liquid crystal polymers by properly combining 2,6-NDA and diol, dicarboxylic acid, and hydroxy dicarboxylic acid.

Light Cycle Oil (LCO), which is one of the by-products of the catalytic cracking gasoline manufacturing process, contains a lot of valuable aromatics such as naphthalene, methylnaphthalene, dimethylnaphthalene, anthracene etc. As explained above, 2,6-DMN in particular, is becoming important as the basic material of PEN, liquid crystal polymer, etc. If it were possible to separate and purify the valuable aromatic hydrocarbons (such as 2,6-DMN) from LCO, which have only been used as fuel mixed with heavy oil, it would be very meaningful in terms of the efficient use of resources.

About 9 wt% of LCO is dimethylnaphthalene (DMN), but 2,6-DMN is just about 0.8 wt% because there are many isomers[1-8]. It is difficult to separate the components by distillation because the boiling points of the ten types of DMN isomers are very similar, as shown in Table 1. Therefore, high-purity 2,6-DMN is produced through a multi-stages process, in which the mixture of DMN isomers in the LCO are enriched by the methods of distillation, extraction, etc., and then the 2,6-DMN is purified by the methods of adsorption[9,10] and crystallization[11-15], making use of the difference in critical dimensions of molecules and melting points of the isomer components in the enriched DMN isomers mixture. We empirically reviewed the enrichment of the DMN isomers, which are included in the LCO, by the combined method of distillation-extraction as the pre-stage toward the high-purity purification of 2,6-DMN in the LCO, and reported the result in the previous work[6].

In this work, we reviewed the high-purity purification of 2,6-DMN as the post-stage, by the combined method of melt crystallization (MC)

for the crude separation of 2,6-DMN contained in the enriched DMN isomers mixture recovered from the LCO by distillation-extraction combination[6,15], and solute crystallization (SC) for high-purity purification of 2,6-DMN contained in the crystal recovered by MC operation. We expected high purity and yield of 2,6-DMN through MC-SC combination. Furthermore, we compared MC - SC combination of this work with SC-SC combination of the previous work[15] in view of the separation process and efficiency of 2,6-DMN.

2. Experimental

2.1. Apparatus and Method

A glass filter produced by Pyrex, with a 6 cm inside diameter and 8 cm height was used in this work[15]. We maintained a constant temperature in the apparatus by circulating the coolant (methanol solution) cooled by the temperature controller in the jacket installed outside the apparatus. A digital thermometer was used to measure the inside temperature of the apparatus, while an aspirator was used for solid-liquid separation.

The specified amount of the raw material (Feed I), or the solution that dissolved a certain amount of crystal 1 (Feed II) in the specified amount of solvent was put into the apparatus, cooled (cooling speed 0.5 °C/min), and reached the particular experimental temperature. The solution reached the experimental temperature was crystallized for a certain time at a constant agitating speed, and then suction filtered for solid-liquid separation in the aspirator. The produced crystal was recovered as it was, or after being washed with the washing solvent (ethanol), which was cooled 2 °C lower than the crystallization operation temperature in advance, to eliminate the remaining liquid that was attached to the crystal. The crystal was dissolved in acetone for determination of the composition, as it was or after the washing solvent evaporated.

GC (Hewlett Packard Co.; HP 6890) equipped with a flame ionization detector (FID) was used in the analysis. Ten kinds of DMN isomers could be separated with the capillary column PLC (30 m × 0.25 mm I.D.). The GC analysis was conducted under carrier gas N₂ (flow velocity 1 mL/min), injection port temperature 300 °C, sample size 2 μL, splitting ratio 100 : 1, initial temperature 120 °C (duration 25 min), temperature rising speed 3 °C/min, and final temperature 200 °C.

2.2. Material System and Conditions

Material system and experimental conditions used in this work are shown in Table 2. The enriched DMN isomers mixture (Feed I) recovered from the LCO by the combined method of distillation and extraction[6,15] was used as the raw material of the MC operation, and the Crystal 1 (Feed II) recovered by the MC operation was used as the raw material of the SC operation. We used the mixed solvent of methanol and acetone (60 : 40 vol%) as the SC solvent, based on both the property of solvent and the balance of purity and the yield of the 2,6-DMN [14].

Table 2. Material System and Experimental Conditions

Melt crystallization (MC)	
Material system	
Feed I :	Enriched DMN isomers mixture (extract** recovered by extraction of distillate*)(6,15)
Experimental conditions	
Impeller speed, N [rpm]	200
Operating temperature, T [°C]	-5~30
Operating time, t [hr]	0.33~3
Solute crystallization (SC)	
Material systems	
Feed II :	Crystal 1***
Solvent :	A mixture of methanol and acetone (60 : 40 vol%)
Washing solvent :	Ethanol
Experimental conditions	
Impeller speed, N [rpm]	200
Operating temperature, T [°C]	-5~30
Operating time, t [hr]	1
Solvent/Feed II volume ratio, S/Feed II [-]	19

* : distillate (temperature range of distillate : 255~277 °C) recovered by batch distillation of LCO, ** : extract recovered by equilibrium extraction (solvent = an aqueous solution of dimethylformamide of distillate), *** : crystal 1 recovered by crystallization (T = 10 °C, N = 200 rpm, t = 1 hr) of Feed I.

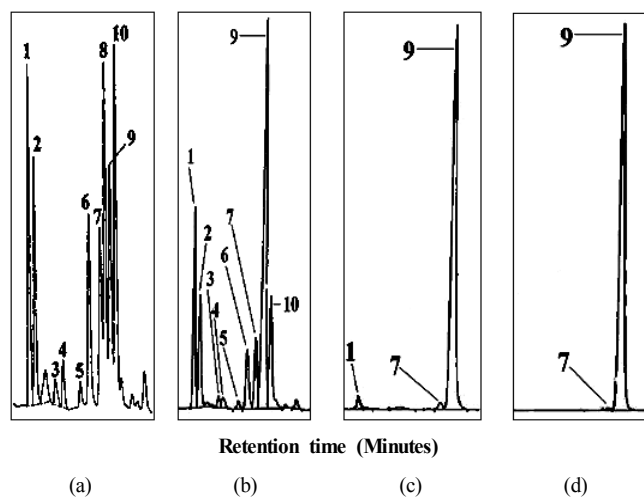


Figure 1. Gas chromatogram of (a) Feed I[6,15], (b) Crystal 1 (Feed II, without washing) obtained by melt crystallization (MC), (c) Crystal 2 (without washing) and (d) Crystal 2 (with washing) obtained by solute crystallization (SC). 1 : 2-methylnaphthalene (2-MN); 2 : 1-MN; 3 : 1-ethylnaphthalene (1-EN); 4 : 2-EN; 5 : diphenyl; 6 : 1,7-dimethylnaphthalene (1,7-DMN); 7 : 2,7-DMN; 8 : 1,3-DMN; 9 : 2,6-DMN; 10 : 1,6-DMN. Recovery conditions of Crystal 1 : T = 10 °C; N = 200 rpm; t = 1 hr. Recovery conditions of Crystal 2 : T = -30 °C; N = 200 rpm; t = 1 hr; S/Feed II = 19.

3. Results and Discussion

Figure 1(a) shows the gas chromatogram of the raw material (Feed I) of MC operation analyzed by GC. Feed I includes 2-methylnaphthalene (2-MN; 16.4 wt%), 1-MN (11.8 wt%), 1-Ethylnaphthalene (1-EN; 1.2 wt%), 2-EN (1.3 wt%), diphenyl (0.9 wt%), 1,7-DMN (7.8 wt%),

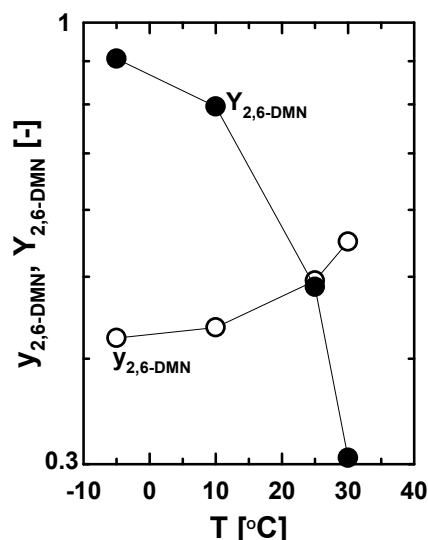


Figure 2. The effect of operating temperature for purification of 2,6-DMN by melt crystallization (MC). Feed used: Feed I. MC conditions : without washing; T = 10 °C; N = 200 rpm; t = 1 h.

2,7-DMN (6.8 wt%), 1,3-DMN (15.8 wt%), 2,6-DMN (10.4 wt%), 1,6-DMN (24.6 wt%), and 3.0 wt% of all others[6,15]. Five other kinds of isomers, excluding the five kinds of DMN isomers identified and quantitatively analyzed in this work, were difficult to identify and quantitatively analyzed because their amount in the raw material was insignificantly small. 10.4 wt% of 2,6-DMN, the target component of this work, contained in Feed I.

Figure 2 shows the effect of the crystallization operating temperature (T) affecting the purity ($y_{2,6-DMN}$) of 2,6-DMN in the crystal recovered from the MC operation and the yield ($Y_{2,6-DMN}$). The yield of 2,6-DMN

at MC operation, $Y_{2,6-DMN}$, is defined as :

$$Y_{2,6-DMN} = \frac{C_1 \times y_{2,6-DMN}(g)}{F_{1,0} \times y_{2,6-DMN,0}(g)}$$

Where C_1 is the weight of the crystal (Crystal 1) obtained after a contact run of MC operation and $F_{1,0}$ is the weight of a raw material (Feed I) at initial of MC operation. $y_{2,6-DMN}$ and $y_{2,6-DMN,0}$ denote the concentration of 2,6-DMN in crystal (Crystal 1) obtained after a contact run of MC operation and that in a raw material (Feed I) at initial of MC operation, respectively. The crystal couldn't be recovered because they all dissolved in washing solvent (ethanol) when the crystals were washed in ethanol cooled 2 °C lower than crystallization operating temperature. This is thought to occur because the crystal is unstable due to the relatively lower purity of 2,6-DMN. Thus, the purities and yields of the 2,6-DMN shown in Figure 2 are the values analyzed when the crystals obtained at each operating temperature are not washed in ethanol. The rise in the operating temperature shows the general tendency of the crystallization operation, in which the purity of 2,6-DMN rises, but the yield decreases. At $T = 30$ °C and $T = -5$ °C, the 2,6-DMN purities were 55% and 44%, respectively, and the yields were 31% and 91%, respectively.

Though the figure is omitted, the review for the effect of the crystallization operating time (t) on the purity and yield of the 2,6-DMN shows that the purities and the yields of the 2,6-DMN were almost the same, regardless of the crystallization operating time ($t = 20, 60, 120, 180$ min). So, the effect of the crystallization operating time on the purity and yield of 2,6-DMN cannot be acknowledged. We could estimate that the crystal formation speed is very fast because the solid-liquid equilibrium was reached within a short time ($t < 20$ min) of crystallization operation.

Figure 1(b) shows the gas chromatogram, which is the GC analysis of Crystal 1, recovered without ethanol washing at the following MC conditions : $T = 10$ °C, $t = 1$ hr, $N = 200$ rpm. The decrease in impurities under MC operation is confirmed, compared with Feed I. About 43.5 wt% of 2,6-DMN was included in Crystal 1.

In order to carry out the high-purity purification of the 2,6-DMN, this work conducted SC operation using Crystal 1 (Feed II) recovered from the MC operation as the raw material, and the mixture of methanol and acetone (60 : 40 vol%) which were chosen based on both the purity and the yield of the 2,6-DMN, as the solvent.

Figure 3 shows the purity and the yield of the 2,6-DMN in Crystal 2, recovered from the SC operation that dissolved Feed II in the mixture of methanol and acetone (60 : 40 vol%) at the following conditions : $T = -30$ °C, $t = 1$ hr, $N = 200$ rpm, Solvent / Feed II volume ratio (S/F II) = 19. The yield of 2,6-DMN at SC operation, $Y_{2,6-DMN}$, is defined as :

$$Y_{2,6-DMN} = \frac{C_2 \times y_{2,6-DMN}(g)}{C_{1,0} \times y_{2,6-DMN,0}(g)}$$

Where C_2 is the weight of the Crystal 2 obtained after a contact run

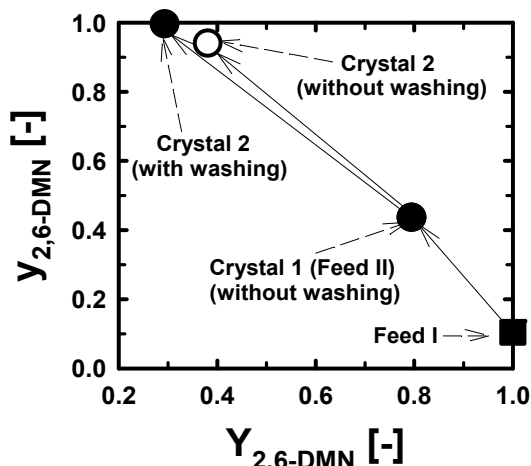


Figure 3. The effect of solute crystallization (SC) and solvent washing for purification of 2,6-DMN. Feed used : Crystal 1 (Feed II); SC solvent used : a mixture of methanol and acetone (60 : 40 vol%); Washing solvent used: ethanol; Recovery conditions of Crystal 1 : $T = 10$ °C; $N = 200$ rpm; $t = 1$ hr. Recovery conditions of Crystal 2 : $T = -30$ °C; $N = 200$ rpm; $t = 1$ hr; S/Feed II = 19.

of SC operation and $C_{1,0}$ is the weight of a raw material (Feed II, Crystal 1) at initial of SC operation. $y_{2,6-DMN}$ and $y_{2,6-DMN,0}$ denote the concentration of 2,6-DMN in crystal (Crystal 2) obtained after a contact run of SC operation and that in a raw material (Feed II, Crystal 1) at initial of SC operation, respectively. This figure also shows the washing effect of ethanol on the Crystal 2 recovered from the SC operation. The purities of the 2,6-DMN in Crystal 2 with washing and without washing are approximately 94 wt% and 99.5 wt%, respectively. The ethanol washing of the crystal confirmed to be effective in improving the purity of the 2,6-DMN, when the purity of the 2,6-DMN in the crystal is over 94 wt%. Based on the amount of 2,6-DMN in Feed I, the yield of the 2,6-DMN in Crystal 2 decreased by about 9 wt% when it was washed, compared to when it wasn't washed. The yield is considered to improve through multi-stages contact using the tower device, and the operation with the optimal SC solvent, washing solvent, and optimal experiment conditions.

Figure 1(c)-(d) show the gas chromatograms of Crystal 2 recovered without ethanol washing and Crystal 2 recovered after ethanol washing. The comparison of (c)-(d) and (a)-(b) shows the decrease in impurities after the SC operation and the washing of crystal. It's been confirmed that the final material (d) recovered from the SC operation includes 99.5 wt% 2,6-DMN and a little tiny amount of 2,7-DMN, which is the impurity. Thus, it is estimated that the final reaction product using the Crystal 2 (d) obtained in this work may include a tiny dosage of 2,7-NDA when the relevant methyl group is converted into carboxylic acid through the oxidation reaction, occurring later on. In polymer's reaction, however, the 2,7-NDA is not expected to cause a decrease in the polymer's molecular weight, which generally occurs due to the impurities included in the monomers, because the 2,7-NDA is the structural isomer of 2,6-NDA (the target material), thus not affecting the equivalent ratio with diol in polymerization. Based on this, we confirmed that the MC-SC combination is one of the very useful

combination in the high-purity purification of 2,6-DMN. The MC-SC process, also, is the simple one without solvent recovery operation for crude separation of 2,6-DMN contained in Feed I, although yield of 2,6-DMN is small, but compared with SC-SC process of the previous work. The yield of 2,6-DMN, however, is expected to be increased by the recycle of the mother liquor. Therefore, the MC-SC process of this work would be a feasible process to purify 2,6-DMN in Feed I.

4. Conclusion

We investigated the high-purity purification of 2,6-DMN contained in the enriched DMN isomers mixture (concentration of 2,6-DMNA : 10.43%) recovered from the LCO by distillation-extraction combination by the combined method of melt crystallization (MC) - solute crystallization (SC). With increasing MC operation temperature, the purity of 2,6-DMN increased sharply, but the yield of 2,6-DMN decreased. At MC conditions of without washing, $T = 30\text{ }^{\circ}\text{C}$ and $T = -5\text{ }^{\circ}\text{C}$, the 2,6-DMN purities were 55% and 44%, respectively, and the yields were 31% and 91%, respectively. At a SC experimental condition fixed (with ethanol washing, $T = -30\text{ }^{\circ}\text{C}$, $t = 1\text{ hr}$, $N = 200\text{ rpm}$, $S/F\text{ II} = 19$), the 2,6-DMN purity was 99.5%, and the yield was about 20% based on the enriched DMN isomers mixture. We confirmed that the MC-SC combination is one of the very useful combination in the high-purity purification of 2,6-DMN contained in the enriched DMN isomers mixture.

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References

1. S. J. Kim, R. Egashira, and J. Kawasaki, Extraction of aromatics in the light cycle oil, - Extraction equilibrium and extraction rate of naphthalene group -, *Sekiyu Gakkaishi*, **38**, 114-120 (1995).
2. S. J. Kim, S. C. Kim, and J. Kawasaki, Separation and purification of 2,6-dimethylnaphthalene in the light cycle oil (I) - Concentration of mixture of dimethylnaphthalene isomers in the light cycle oil, *Appl. Chem. Eng.*, **7**, 162-170 (1996).
3. S. J. Kim, S. C. Kim, and J. Kawasaki, Separation and purification of 2,6-dimethylnaphthalene in the light cycle oil (II) - Separation of individual isomers of dimethylnaphthalene -, *Appl. Chem. Eng.*, **7**, 869-876 (1996).
4. S. J. Kim and D. H. Kim, Separation of aromatics in light cycle oil by solvent extraction - Re-extraction of aromatics in extract phase -, *Appl. Chem. Eng.*, **8**, 967-972 (1997).
5. S. J. Kim, S. C. Kim, and H. K. Bae, Comparison of liquid membrane permeation with solvent extraction on separation of valuable aromatics in light cycle oil, *Membrane Journal*, **8**, 138-147 (1998).
6. S. J. Kim and S. C. Kim, Separation and recovery of dimethylnaphthalene isomers from light cycle oil by distillation-extraction combination, *Sep. Sci. Technol.*, **38**, 4095-4116 (2003).
7. S. J. Kim and S. C. Kim, Separation of valuable bicyclic aromatic components from light cycle oil by an emulsion liquid membrane, *Sep. Sci. Technol.*, **39**, 1093-1109 (2004).
8. S. J. Kim, S. C. Kim, and J. Kawasaki, Separation and recovery of bicyclic aromatic components in the light cycle oil, *Sep. Sci. Technol.*, **38**, 179-199 (2003).
9. H. Uchida, Y. Iwai, M. Amiya, and Y. Arai, Adsorption behaviors of 2,6- and 2,7-dimethylnaphthalenes in supercritical carbon dioxide using NaY-type zeolite, *Ind. Eng. Chem. Res.*, **36**, 424-429 (1997).
10. J. P. Verduijn, M. J. G. Janssen, C. B. De Gruijter, W. T. Koetsier, and C. W. M. Van Oorschot, Process for separation dimethylnaphthalene isomers with zeolite L agglomerates, U. S. Patent, 5,146,040 (1992).
11. M. Motoyuki, K. Yamamoto, S. Yoshida, S. Yamamoto, A. V. Sapre, J. P. McWilliams, S. P. Donnelly, and S. D. Hellring, Isomerization of dimethylnaphthalene to produce 2,6-dimethylnaphthalene, U. S. Patent, 6,018,087 (2000).
12. M. Motoyuki, K. Yamamoto, A. V. Sapre, J. P. McWilliams, and S. P. Donnelly, Process for preparing 2,6-dimethylnaphthalene, U. S. Patent, 6,018,086 (2000).
13. M. Motoyuki, K. Yamamoto, J. P. McWilliams, and R. G. Bundens, Process for Preparing dialkylnaphthalene, U. S. Patent, 5,744,670 (1998).
14. M. Motoyuki, K. Yamamoto, A. V. Sapre, and J. P. McWilliams, Process for Preparing dialkylnaphthalene U. S. Patent, 6,011,190 (2000).
15. S. J. Kim and H. J. Jeong, High-purity purification of 2,6-dimethylnaphthalene (2,6-DMN) in light cycle oil - Purification of 2,6-DMN from concentrate of DMN isomers by crystallization -, *Appl. Chem. Eng.*, **19**, 105-110 (2008).