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Separation and Recovery of Bicyclic Aromatic Components in the Light Cycle Oil

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ABSTRACT

There are a lot of valuable aromatic components in light cycle oil (LCO). Among them, 2,6-dimethylnaphthalene is focused as the elementary raw material for engineering plastic (PEN plastic) and polymer liquid crystal, etc. We investigated the separation and recovery of valuable aromatic components (bicyclic aromatic components: carbon number 10–12) in LCO by solvent extraction method. Sulfolane, dimethylsulfoxide (DMSO), diethyleneglycol, and dimethylformamide were used as extraction solvents to measure distribution equilibrium. It was found that DMSO was a promising extraction solvent based on the distribution coefficient of bicyclic aromatic component and selectivity for n-Nonane.

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The effect of operation factors on extraction performance for bicyclic aromatic components in LCO using DMSO as extraction solvent was also studied. With increasing moisture content of solvent, the distribution coefficient of bicyclic aromatic components decreased and selectivity increased. Increasing operation temperature resulted in decreasing the distribution coefficient and selectivity. The lower the carbon number, the higher the distribution coefficient and selectivity of bicyclic aromatic components. Because boiling temperature of DMSO overlapped with that of component, it was difficult to recover extract component of extract phase. Benzene, toluene, m-xylene, n-hexane (HX), and n-octane were used as secondary solvents, and the distribution equilibrium between extract phase (re-extraction feed) and secondary solvent was measured. It was found that HX was a promising solvent for recovering bicyclic aromatic components. To examine the effect of operation factors on recovering bicyclic aromatic components, HX was used as a re-extraction solvent. The distribution coefficient of bicyclic aromatic components decreased smoothly while increasing the mass ratio of solvent to re-extraction feed and operation temperature. The higher the carbon number, the higher the distribution coefficient of bicyclic aromatic components. To examine the process of separation and recovery for dimethylnaphthalene mixture with 10 structural isomers in the LCO, the experiment result obtained from equilibrium extraction and equilibrium re-extraction were used.

Key Words: Light cycle oil (LCO); Bicyclic aromatic components; Dimethylnaphthalene; Solvent extraction; Distribution equilibrium; Separation process.

INTRODUCTION

Recently, it is stressed that petroleum is used as a raw material rather than energy in view of efficient resource utilization. LCO, specifically, which includes lots of raw materials, is used only as a fuel. 2,6-dimethylnaphthalene (2,6-DMNA) in LCO is paid attention as raw materials for engineering plastic (PEN plastic), polymer liquid crystal, etc. Therefore, it is very significant that valuable aromatic hydrocarbons such as 2,6-DMNA in LCO can be separated and recovered by dearomatization of LCO. Also, as the cetane number of raffinate oil can be improved by dearomatization of LCO, it may be used as diesel oil.

Extraction method using solvent such as sulfolane (SUL) and diethylene glycol (DEG), etc.,[1–8] is mainly used for separating aromatic groups from petroleum products with low boiling temperature such as naphtha and gasoline. In solvent extraction of aromatic components in LCO, solvents such as SUL and DEG are difficult to recover by distillation alone after extraction operation because the boiling point between extraction solvent and extract component overlap. Therefore, there are few solvent extraction reports for dearomatizing of petroleum product with high boiling temperature such as LCO.

Alvin L Benham et al.[9] reported dearomatization of LCO by solvent extraction. They used the mixture of furfural and water as an extraction solvent for dearomatizing of LCO, and the mixture of xylene and naphtha as a re-extraction solvent for recovering extract components in the extract phase, i.e., redex process. This process was for mainly improving the cetane number of raffinate oil and, subsequently, experimental review on separating and recovering each aromatic component by extraction and re-extraction was found to be unsatisfactory.

In the previous work,[10,11] we investigated separation of valuable bicyclic aromatic components (carbon number 10–12) in LCO by solvent extraction method. The distribution equilibrium between LCO and solvent was measured by using SUL, DMSO, DEG, and DMF as extraction solvent. DMSO was found to be a suitable solvent to extract bicyclic aromatic components in LCO. Furthermore, the effect of operation factors on separating bicyclic aromatic components was investigated by equilibrium extraction using DMSO. With increasing the moisture content in solvent, the distribution coefficient of bicyclic aromatic components decreased and the selectivity based on n-nonane increased. Increasing operation temperature resulted in decreasing the distribution coefficient and the selectivity of bicyclic aromatic component. The lower the carbon number, the higher the distribution coefficient and the selectivity based on n-nonane. Extraction operation resulted in increasing the paraffin concentration of raffinate phase, and subsequently increasing the cetane number of raffinate phase. It appeared that it could be used as diesel oil.

Because boiling temperature of DMSO used as equilibrium extraction solvent of the previous work was similar to that of extract component, it was difficult to recover extract component in extract phase by distillation alone. Therefore, in this work, the recovery of bicyclic aromatic components in extract phase was investigated by re-extraction operation using secondary solvents. Considering boiling points of solvent and extract components, secondary solvents, which were aromatic component (benzene, toluene, m-xylene) and paraffine component (n-hexane, n-octane), were applied to possibly form the two liquid phases. Distribution equilibrium was measured using solvent forming two liquid phases, and optimum solvent for recovery of bicyclic aromatic component in extract phase was surveyed. Re-extraction by optimum solvent was performed, and the effect of operation factors on recovering bicyclic aromatic components was studied. We also examined the processes of separation and recovery for dimethylnaphthalene (DMNA) mixture with 10 structural isomers in LCO using the experiment result of equilibrium extraction of the previous work and that of the equilibrium re-extraction of this work.

EXPERIMENTAL METHOD

Equilibrium Extraction[10,11]

GC capillary column was used to analyze components of LCO in this work. It was difficult to quantify paraffin components (carbon number 11–25) in LCO because the peak of paraffin components overlapped with the peak of aromatic components.

We investigated the separation between bicyclic aromatic components and paraffin components using LCO A (LCO added a little bit of n-nonane [carbon number 9]) and LCO B (LCO added a little bit of n-heptane [carbon number 7], n-octane [carbon number 8] and n-nonane, respectively) as feed. From these results, we could estimate the separation of bicyclic aromatic component and paraffin component.

To make solvent normal concentration, city water was added into each SUL, DMSO, DEG, and DMF, respectively, and mixed. Then the solvent was placed into 200 ml of Erlenmeyer flask and was moved into vibration hot bath kept at experimental temperature. After the solvent reached experimental temperature, the feed (LCO A, LCO B) kept at experimental temperature was added. The solvent and the feed were contacted at vibration hot bath for 48 h and then they reached equilibrium. Vibration stopped at equilibrium. They were set to constant time, and then raffinate phase and extract phase were separated by separatory funnel. Recovered raffinate phase could not be analyzed because of gas chromatogram of solvent and raffinate oil overlapping. Therefore, 50 ml of tap water was added into 50 ml of raffinate phase and they were stirred with magnetic stirrer at room temperature for 1 h to remove the solvent in raffinate phase, and then raffinate oil could be analyzed. To quantify the solvent in raffinate phase, acetone was added into the aqueous solution containing solvent made from washing raffinate phase. For extract phase, 120 ml of city water and 20 ml of n-haxane were added into 20 ml of extract phase and they were contacted and stirred for 1 h. Extract components were re-extracted with n-haxane and then this oil phase was analyzed.

Equilibrium Re-extraction

Extract phase, which was obtained by equilibrium extraction operation under the condition of Table 1, was used as the feed of equilibrium re-extraction. Feed was put into 200 ml of Erlenmeyer flask and then it was placed in vibration hot bath kept at experimental temperature. After feed reached experimental temperature, the solvent held at experimental temperature was added into it. They were place in a contacted vibration hot bath for 48 h and reached equilibrium. After they reached equilibrium, vibration stopped, constant time set, and then raffinate phase and extract phase were separated by separatory funnel.

Analyzing method of extract phase obtained by re-extraction operation was equivalent to that of extract phase obtained by equilibrium extraction

Table 1. Systems and experimental conditions.

Equilibrium extraction[10,11]	
Systems	
Feeds:	
Light cycle oil (LCO), LCO A, LCO B	
Solvents:	
1) Sulfolane (SUL), SUL aqueous solution	
2) Dimethylsulfoxide (DMSO), DMSO aqueous solution	
3) Diethyleneglycol (DEG), DEG aqueous solution	
4) Dimethylformamide (DMF), DMF aqueous solution	
Conditions	
Mass fractions of water in solvent at initial, $y_{w,0}$[-]	0 ∼ 0.08
Operating temperatures, T [°C]	30 ∼ 52
Operating time, t [hr]	48
Solvent/feed mass ratios, S/F [−]	1 ∼ 10
Equilibrium re-extraction	
Systems	
Feed:	
Extract phase[a]	
Solvents:	
1) Aromatics (benzene, toluene, m-xylene [mXL])	
2) Paraffins (n-hexane [HX], n-octane [OT])	
Conditions	
Operating temperatures, T [°C]	18 ∼ 40
Operating time, t [hr]	48
Solvent/feed mass ratios, S/F [−]	0.27 ∼ 5.56

[a] Extract phase obtained by equilibrium extraction operation of $y_{w,0} = 0.03$, T = 30°C and S/F = 1 using DMSO aqueous solution.

operation. However, it was needed to quantify the solvent in raffinate phase in analyzing raffinate phase. 120 ml of city water and 20 ml of n-hexane (or n-heptane) corresponding to the re-extraction solvent used were added into 20 ml of raffinate phase, and then were stirred. Each component in raffinate phase was re-extracted by n-hexane or n-heptane and they were analyzed. An analysis of raffinate phase and extract phase was carried out by a gas chromatograph equipped with flame ionization detector (FID). ULBON HR-1 capillary column was used. Material systems and experimental conditions of each operation were summarized in Table 1. Each different equilibrium state could be obtained by varying the mass ratio of solvent to feed.

RESULT AND DISCUSSION

Gas Chromatogram of LCO

Total mass of Aromatic components in LCO is 60–80 wt%. The paraffin components are balanced and olefin component is negligible. In LCO are mono, bi, and tricyclic aromatic components as aromatic components. Monocyclic aromatic components are alkyl benzene and indane group. Bicyclic aromatic components are napththalene, biphenyl, and fluolene group. Tricyclic aromatic components are anthracene group.

Fig. 1 shows gas chromatogram of LCO A.[10,11] Peak 2 was napththalene and peak 7 was phenanthrene. These indicated that LCO contained a lot of mono and bicyclic aromatic components. DMNA with 10 structural isomers represented five peaks. However, in this work their concentrations were summed in all and were considered as one component. Table 2 shows the composition of hydrocarbon in LCO.[10,11]

Definition Equations

The distribution coefficient, m_i, the ratio of composition for component *i* in extract phase to that in raffinate phase, is defined as:

$$m_i = y_i/x_i \tag{1}$$

where y_i and x_i, respectively, denote the mass fraction of component *i* in the extract phase and that in the raffinate phase after a run.

Yield of component *i*, Y_i, is defined as:

$$Y_i = Ey_i/R_o x_{i,0} \tag{2}$$

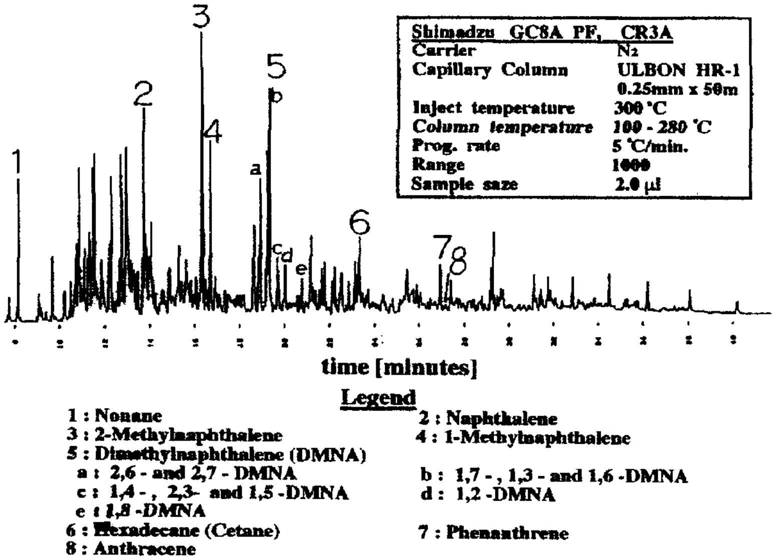


Figure 1. Gas chromatogram of LCO A.[10,11]

Table 2. Composition of feed used at equilibrium extraction operation.[10,11]

	Mass fraction		
Component	LCO	LCO A	LCO B
n-heptane	0	0	0.005
n-octane	0	0	0.005
n-nonane	0	0.005	0.005
Naphthalene (NA)	0.01218	0.01212	0.01200
1-methylnaphthalene (1MNA)	0.01165	0.01159	0.01148
2-methylnaphthalene (2MNA)	0.02604	0.02591	0.02565
A mixture of 10 isomers of dimethylnaphthalen (DMNAs)	0.05120	0.05097	0.05043
a: 2,6- and 2,7-DMNA mixture	0.01440	0.01434	0.01418
b: 1,7-, 1,3-, and 1,6-DMNA mixture	0.02194	0.02184	0.02161
c: 1,4-, 2,3-, and 1,5-DMNA mixture	0.00682	0.00560	0.00555
d: 1,2-DMNA	0.00563	0.00560	0.00555
e: 1,8-DMNA	0.00241	0.00240	0.00237

where $x_{i,0}$ denotes the mass fraction of component *i* in the feed. E refers to the mass of the extract phase after a run and R_o denotes the mass of the feed.

Selectivity of component *i*, $\beta_{i,j}$, the ratio of the distribution coefficient for component *i* to that for component *j*, was calculated from Eq. (3).

$$\beta_{i,j} = m_i/m_j \tag{3}$$

Mass balance of component *i* was checked by using Eq. (4) as follows:

$$R_o x_{i,0} + E_o y_{i,0} = R x_i + E y_i \tag{4}$$

Where E_o and R, respectively, denote the initial mass of extract phase and that of raffinate phase after a run. Mass balance of all components checked at extraction and re-extraction operation was satisfactory.

Equilibrium Extraction

Comparison of Solvent

Fig. 2 shows the comparison of solvent on the distribution coefficient of naphthalene (NA) and the selectivity of NA in reference to n-nonane (NO).[10,11] The sequence of m_{NA} was DMF > DMSO > SUL > DEG and the sequence of $\beta_{NA,NO}$ was DMSO > SUL ≒ DEG > DMF. This result of NA was equivalent to the result of 1-methylnaphthalene (1MNA), 2-methylnaphthalene (2MNA) and the mixture of 10 DMNA isomers (DMNAs). Therefore, DMSO was found to be an optimum solvent for extracting bicyclic aromatic components in LCO based on the distribution coefficient and selectivity.

Equilibrium Extraction with DMSO

Fig. 3 shows the effect of S/F on m_i and $\beta_{i,NO}$. With increasing S/F, m_i decreased. Although such a phenomenon is normal for solvent extraction, the effect of S/F on $\beta_{i,NO}$ was negligible. At constant S/F, the lower the carbon number, the higher the distribution coefficient. This result agreed with the solubilities of each components in solvent. In the case of the same carbon number, the distribution coefficient of 1MNA was slightly higher than that of 2MNA. Also, the lower the carbon number of bicyclic aromatic component, the higher the selectivity. The selectivity of 1MNA was slightly higher than that of 2MNA of the same carbon number. At S/F = 1 the yields of NA,

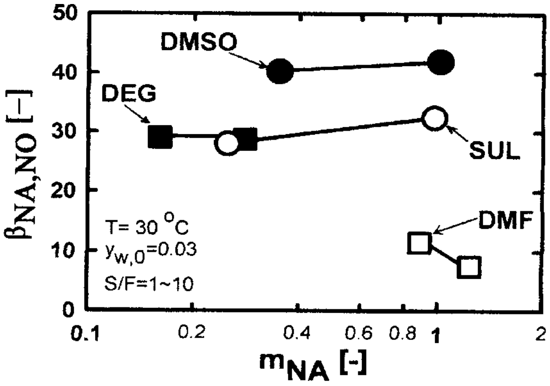


Figure 2. Comparison of solvent on distribution cofficient of naphthalene and selectivity of naphthalene in reference to n-nonane.[10,11] Feed used: LCO A, NA: naphthalene, NO: n-nonane, DMSO: dimethylsulfoxide, DEG: diethyleneglycol, SUL: sulfolane, DMF: dimethylformamide.

1MNA, 2MNA, DMNAs calculated by using Eq. (2) were 0.59, 0.47, 0.43, 0.30, respectively. At S/F = 10 the yields of NA, 1MNA, 2MNA, DMNAs were 0.96, 0.86, 0.83, 0.69, respectively (see Table 4). These results indicated that S/F = 1 was favorable to extracting bicyclic aromatic components in LCO when cost for recovery of solvent was considered.

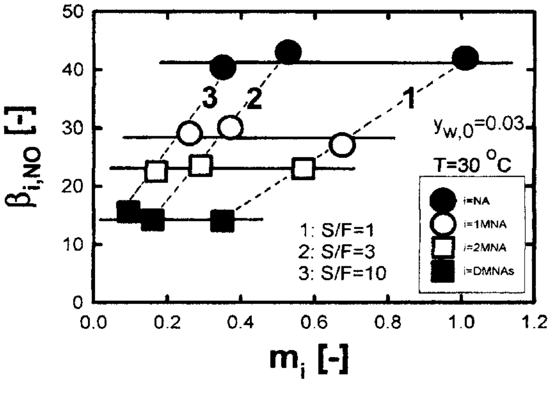


Figure 3. Effects of ratio of solvent-to-feed on distribution coefficient and selectivity of bicyclic aromatic component. Feed used: LCO A, solvent used: DMSO aqueous solution, 1MNA: 1-methylnaphthalene, 2MNA: 2-methylnaphthalene, DMNAs: dimethylnaphthalene mixture with ten structural isomers.

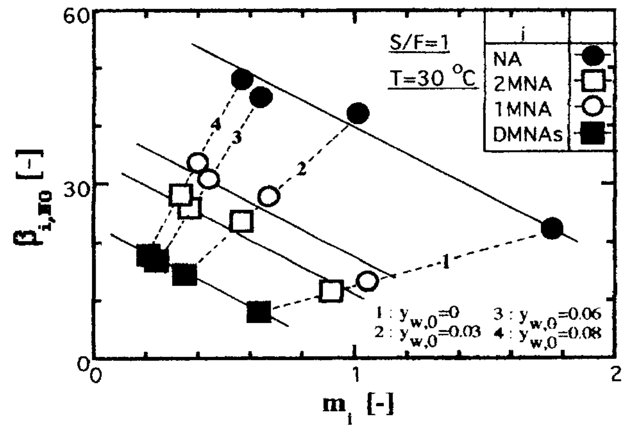


Figure 4. Effects of moisture content in solvent on distribution coefficient and selectivity of bicyclic aromatic component.[10,11] Feed used: LCO A, solvent used: DMSO aqueous solution.

Fig. 4 shows the effect of the moisture content in solvent ($y_{w,0}$) at initial on m_i and $\beta_{i,NO}$.[10,11] With increasing $y_{w,0}$, m_i decreased, but $\beta_{i,NO}$ increased. This result is normal for solvent extraction. At $y_{w,0} = 0$ the yields of NA, 1MNA, 2MNA, DMNAs were 0.83, 0.68, 0.63, and 0.47, respectively. At $y_{w,0} = 0.08$ the yields of NA, 1MNA, 2MNA, and DMNAs were 0.46, 0.32, 0.30, 0.18, respectively (see Table 4). Considering the yield and the selectivity for each component, $y_{w,0} = 0.03$ is favorable to extracting naphthalene group.

Fig. 5 shows m_i and $\beta_{i,NO}$ as a temperature parameter.[10,11] With increasing operation temperature, m_i and $\beta_{i,NO}$ decreased. At T = 30°C the yields of NA, 1MNA, 2MNA, and DMNAs were 0.59, 0.47, 0.43, and 0.30, respectively. At T = 52°C the yields of NA, 1MNA, 2MNA, and DMNAs were 0.62, 0.50, 0.47, and 0.32, respectively. These results indicated that yields were independent of operation temperature (see Table 4). From the results of the yield and selectivity for bicyclic aromatic components based on operation temperature, it is expected that the solvent extraction of naphthalene group in LCO can be operated at room temperature.

Fig. 6. shows the relationship between the selectivity of aromatic-paraffin or same group (aromatic-aromatic or paraffin-paraffin) and the carbon number of hydrocarbon component obtained with LCO B as feed.[11] With using NO as a reference component, the selectivity of aromatic components was much higher than that of paraffin. Also, bicyclic aromatic components could be easily separated from paraffin components with increasing carbon number of

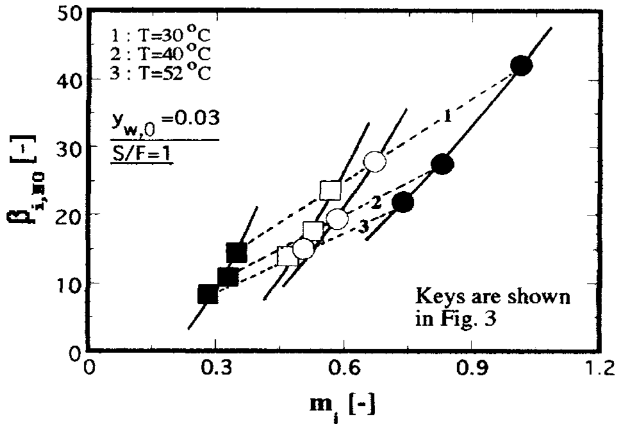


Figure 5. Effects of operation temperature on distribution coefficient and selectivity of bicyclic aromatic component.[10,11] Feed used: LCO A, solvent used: DMSO aqueous solution.

paraffin. The selectivities of n-heptane and n-octane with using NO as reference indicated that the higher the carbon number of paraffin component, the lower the solubility of solvent. In reality, the carbon number of paraffin components in LCO were from 2 to 16 higher than that of NO. Therefore, even

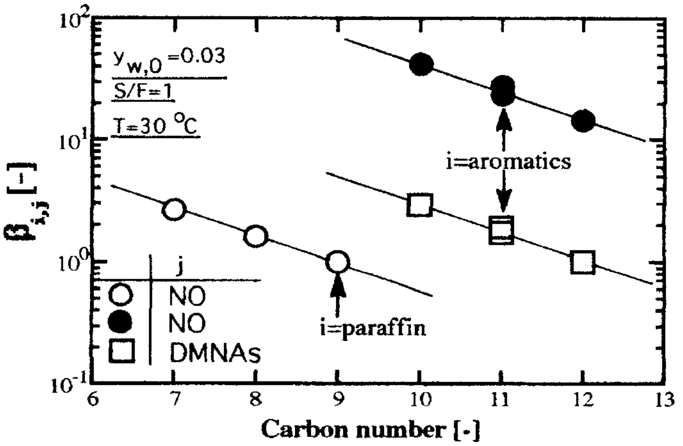


Figure 6. Effects of carbon number on selectivity of hydrocarbons in feed.[11] Feed used: LCO B, solvent used: DMSO aqueous solution.

though any paraffin in LCO was used as a reference component, it was expected that the selectivities were higher than those with using NO as reference. These results suggested that the selectivity of all aromatic components mixture in reference to all paraffin components mixture in LCO could be very high. DMSO extraction was found to be a promising method in dearomatizatin of LCO. Among aromatic components with different carbon number, the bigger the difference in carbon number, the easier the separation. However, the selectivities among aromatic components with the same carbon number were observed to be unit, and it was difficult to separate between isomer components.

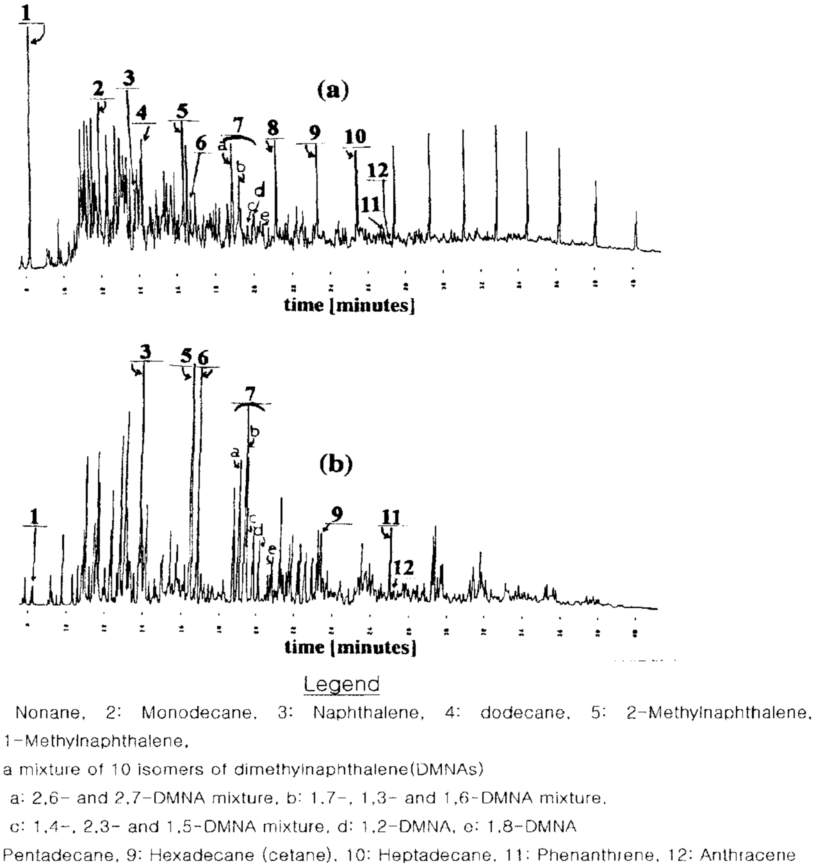
The Gas Chromatogram of Raffinate Phase and Extract Phase

Fig. 7(a) and (b) show the gas chromatogram of raffinate phase and extract phase without solvent.[11] The gas chromatogram of raffinate phase was very different from that of LCO A. Extracting aromatic components by extraction operation resulted in decreasing the peaks of aromatic components, and subsequently increasing those of paraffin components. These results suggested that it could be used as diesel oil of raffinate phase without solvent, expecting that the cetane number of raffinate phase increased. Also, LCO used in this study included heavy paraffin which was 11 to 25 of carbon number. When the gas chromatogram of extract phase was compared with that of feed (LCO A), the peaks of bi- and tri-aromatic components and the other aromatic component were supposed to be increased.

Equilibrium Re-extraction

The Composition of Re-extraction Feed

Extract phase, obtained by equilibrium extraction of LCO, was used as feed of re-extraction operation. The composition of bicyclic aromatic components in feed was summarized in Table 3. 1,8-dimethylnaphthalene (1,8-DMNA) in feed was impossible to analyze quantitatively. Therefore, in this work the total concentration of DMNA except 1,8-DMNA was considered as concentration of DMNAs. It was difficult to measure the amount of paraffin component in extract component due to the overlapped peaks between paraffin components and aromatic components.



Legend

1: Nonane, 2: Monodecane, 3: Naphthalene, 4: dodecane, 5: 2-Methylnaphthalene,
6: 1-Methylnaphthalene,
7: a mixture of 10 isomers of dimethylnaphthalene(DMNAs)
  a: 2,6- and 2,7-DMNA mixture, b: 1,7-, 1,3- and 1,6-DMNA mixture,
  c: 1,4-, 2,3- and 1,5-DMNA mixture, d: 1,2-DMNA, e: 1,8-DMNA
8: Pentadecane, 9: Hexadecane (cetane), 10: Heptadecane, 11: Phenanthrene, 12: Anthracene

Figure 7. Gas chromatogram of (a) extract phase and (b) raffinate phase without solvent obtained by equilibrium extraction of $y_{w,0} = 0.03$, $S/F = 6$ and $T = 30°C$.[11] Feed used: LCO A, solvent used: DMSO aqueous solution.

Comparison of Solvent

When monocyclic aromatic components (benzene [BZ], toluene [TL], m-xylene [mXL]) and paraffin components (n-hexane [HX], n-octane [OT]) were used as solvent, the possibility of forming two liquid phases was investigated. In the case of using BZ and TL, two liquid phases were unformed under the experimental condition of this work and in the case of using mXL, two liquid phases unformed at $S/F < 1$.

Table 3. Composition of feed[a] used at equilibrium re-extraction operation.

Component	Mass fraction
Naphthalene (NA)	0.005200
1-methylnaphthalene (1MNA)	0.004427
2-methylnaphthalene (2MNA)	0.016900
A mixture of 10 isomers of dimethylnaphthalene (DMNAs)	0.013367
a: 2,6- and 2,7-DMNA mixture	0.003710
b: 1,7-, 1,3-, and 1,6-DMNA mixture	0.006600
c: 1,4-, 2,3-, and 1,5-DMNA mixture	0.001924
d: 1,2-DMNA	0.001133

[a] Extract phase obtained by equilibrium extraction operation of $y_{w,0} = 0.03$, $S/F = 1$ and $T = 30°C$ using DMSO aqueous solution.

Table 4. Yield of bicyclic aromatic component obtained from each operation.

	Yield of bycyclic aromatic component					
	Parameter		NA	1MNA	2MNA	DMNAs
Equilibrium extraction	S/F [-] ($y_{w,0} = 0.03$, $T = 30°C$)	1	0.59	0.47	0.43	0.30
		3	0.66	0.55	0.52	0.37
		6	0.81	0.65	0.61	0.51
		10	0.96	0.86	0.83	0.69
	$y_{w,0}$[−] ($S/F = 1$, $T = 30°C$)	0	0.83	0.68	0.63	0.47
		0.03	0.59	0.47	0.43	0.30
		0.06	0.51	0.37	0.34	0.23
		0.08	0.46	0.32	0.30	0.18
	T [°C] ($y_{w,0} = 0.03$, $S/F = 1$)	30	0.59	0.47	0.43	0.30
		40	0.60	0.48	0.45	0.31
		52	0.62	0.50	0.47	0.32
Equilibrium re-extraction	S/F [−] ($T = 30°C$)	0.27	0.28	0.32	0.36	0.45
		0.6	0.40	0.46	0.48	0.54
		2.5	0.63	0.67	0.67	0.77
		5.5	0.72	0.75	0.76	0.78
	T [°C] ($S/F = 0.27$)	18	0.29	0.33	0.40	0.47
		30	0.28	0.32	0.36	0.45
		40	0.26	0.33	0.38	0.43

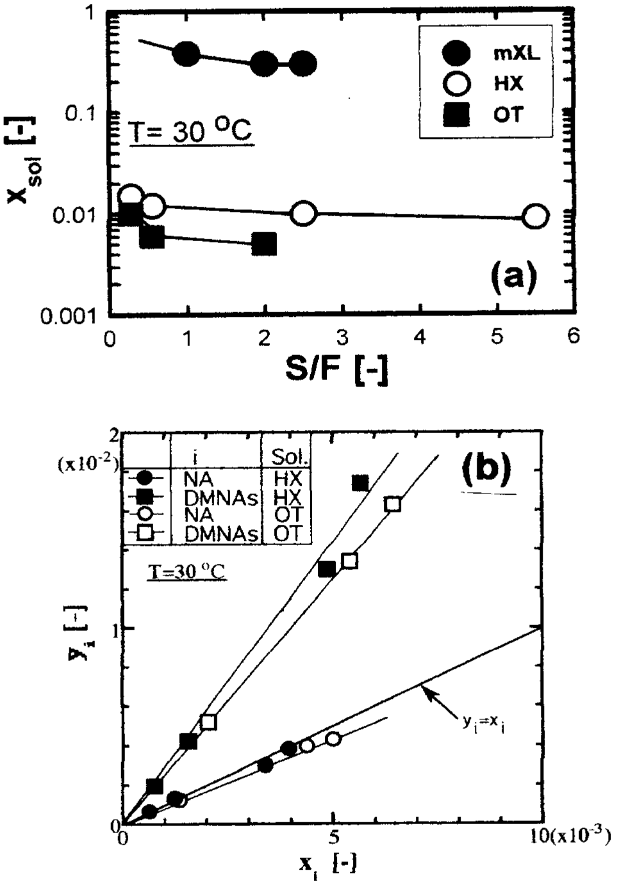


Figure 8. Solvent comparison for (a) mass fraction of solvent in raffinate phase and (b) distribution coefficient of naphthalene and dimethylnaphthalene mixture with 10 structural isomers. Feed used: extract phase obtained by equilibrium extraction between LCO and DMSO aqueous solution at $y_{w,0} = 0.03$, $S/F = 1$ and $T = 30°C$. mXL: m-xylene, HX: n-hexane, OT: n-octane.

Fig. 8(a) and (b) show the results of the recovery for bicyclic aromatic components with HX, OT, and mXL($S/F > 1$). Fig. 8(a) shows the relationship between mass fraction of each solvent in raffinate, phase (x_{sol}) and S/F. The sequence of x_{sol} was mXL > HX > OT. These results corresponded to the solubilities of each solvent into the feed of re-extraction. Namely, carbon number of HX is two smaller than that of OT between paraffin components. Therefore, the solubility of HX is higher than that of OT into the feed of re-extraction. Also, when the carbon number of HX (paraffin components) subtracted from that of mXL (aromatic components), the value was 2. This result indicated that the solubility of mXL was higher than that of HX into the feed of re-extraction.[12] Raffinate phase contained 40% of mXL in the case of using mXL. Considering the recovery of solvent by distillation from this result, mXL was unfavorably economic comparing to HX and OT. The result of mXL suggested that the liquid mixture of aromafic components (carbon number is less than 11) in LCO could be used as re-extraction solvent for recovery of DMNAs in the feed of re-extraction. Fig. 8(b) shows the distribution coefficient (m_i) of each bicyclic aromatic component comparing with HX and OT. Irrespective of solvent, m_i was placed on the straight line. The m_i of HX was higher than that of OT. These results suggested that when the solvent was recovered by distillation with different boiling points of solvent, HX, rather than OT, was found to be a promising solvent.

Equilibrium Re-extraction with n-Hexane

Fig. 9(a) and (b) show the effects of S/F and operation temperature on the distribution coefficient of bicyclic aromatic component, respectively. The distribution coefficient of each component was decreased smoothly with increasing S/F and operation temperature. In extracting aromatic components in LCO, the more the carbon number of component which was difficult to dissolving in extract solvent of LCO (DMSO), the easier the re-extraction. Therefore, in contrast with the results of equilibrium extraction operation of LCO, the distribution coefficient sequence of each component was DMNAs $>$ 2MNA $>$ 1MNA $>$ NA. The yield by re-extraction was calculated using Eq. (2) defined as the mass ratio of each component in extract phase obtained by re-extraction to each bicyclic aromatic component in the feed. At S/F $= 0.27$ the yields of NA, 1MNA, 2MNA, and DMNAs were 0.28, 0.32, 0.36, and 0.45, respectively. At S/F $= 5.5$ the yields of NA, 1MNA, 2MNA, and DMNA were 0.72, 0.75, 0.76, and 0.78, respectively (see Table 4). These results indicated that increasing S/F resulted in increasing yields. From the yields of each component according to S/F, it was thought that re-extraction operated at S/F $= 0.27$ was favorable to the recovery ratio of bicyclic aromatic component per unit volume of re-extraction solvent. Also, at T $= 18$°C the yields of NA, 1MNA, 2MNA, and DMNAs were 0.29, 0.33, 0.40, and 0.47, respectively. At T $= 40$°C the yields of NA, 1MNA, 2MNA, and DMNAs were 0.26, 0.33, 0.38, and 0.43, respectively (see Table 4). The yield was constant and independent of operation temperature. Therefore,

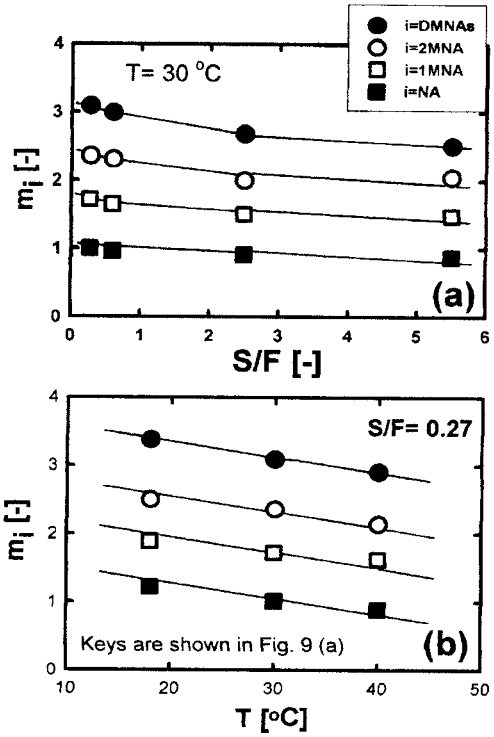


Figure 9. Effects of (a) ratio of solvent-of-feed and (b) operation temperature on distribution coefficient. Feed used: extract phase obtained by equilibrium extraction between LCO and DMSO aqueous solution at $y_{w,0} = 0.03$, S/F = 1 and T = 30°C, solvent used: n-hexane.

naphthalene group component in the feed of re-extraction could be recovered at room temperature.

The Process for Separation and Recovery of DMNAs in LCO

Fig. 10(a) and (b) show the recovery process of DMNAs in LCO. Fig. 10(a) shows the process using HX as re-extraction solvent, and Fig. 10(b) shows the process using the mixture of aromatic components (carbon number is less than 11) in LCO suggested as re-extraction solvent in Fig. 8(a). Fig. 10(a) consists of the extraction column for aromatic group ⟨1⟩, the re-extraction column for aromatic group ⟨2⟩, the washing column for re-extraction solvent (HX) including

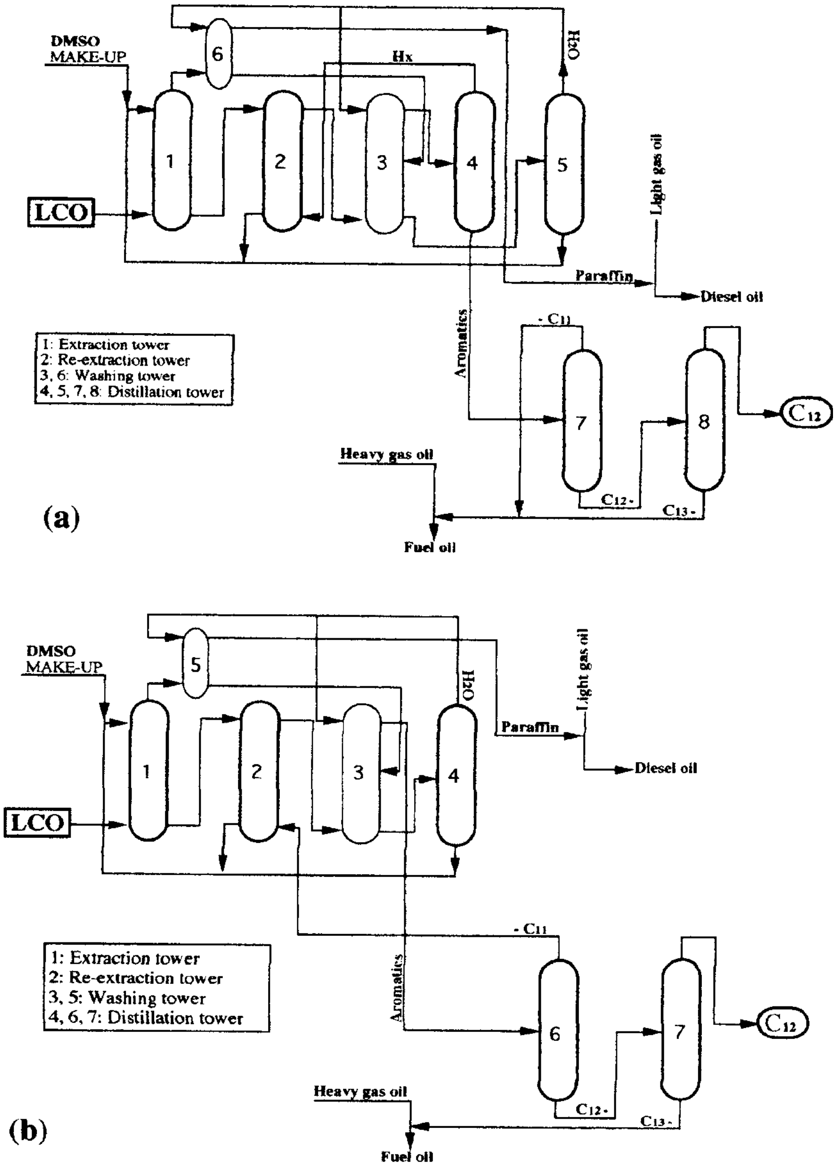


Figure 10. Simplified process on recovery of DMNAs in LCO, (a) in case of using n-hexane as re-extraction solvent, (b) in case of using liquid aromatics mixture less than carbon number 11 in LCO as re-extraction solvent.

aromatic components ⟨3⟩, the distillation column for recovering re-extraction solvent ⟨4⟩, the distillation column for recovering extraction solvent (DMSO) ⟨5⟩, the washing column of paraffin phase ⟨6⟩, and two distillation towers for recovery of DMNAs in aromatic components ⟨7, 8⟩. Fig 10(b) omits the distillation for recovering re-extraction solvent from Fig. 10(a). However, the mixture of aromatic components (carbon number is less than 11), which come from the top of the distillation column ⟨6⟩ for recovery of aromatic components more than carbon number 12, was used as re-extraction solvent and fed to the bottom of re-extraction column ⟨2⟩ for aromatic components.

CONCLUSION

1. The distribution equilibrium between LCO and solvent was measured by using SUL, DMSO, DEG, and DMF as extraction solvent. DMSO was found to be a suitable solvent to extract bicyclic aromatic components in LCO. The effect of operation factors on recovering bicyclic aromatic components was investigated by equilibrium extraction using DMSO. With increasing the moisture content in solvent, the distribution coefficient of bicyclic aromatic components decreased and the selectivity based on n-nonane increased. Increasing operation temperature resulted in decreasing the distribution coefficient and the selectivity of bicyclic aromatic component. The lower the carbon number, the higher the distribution coefficient and the selectivity based on n-nonane. Extraction operation resulted in increasing the paraffin concentration of raffinate phase, and subsequently increasing the cetane number of raffinate phase. Therefore, it was found that raffinate phase could be used as diesel oil.
2. The possibility of forming two liquid phases was investigated by using extract phase obtained from equilibrium extraction of LCO as re-extraction feed and benzene, toluene, m-xylene, n-hexane and n-octane as re-extraction solvent. In the case of using n-Hexane, n-octane and m-xylene($S/F > 1$), two liquid phases were formed. The distribution equilibrium between extract phase and solvent was measured with the re-extraction solvent of which two liquid phases were formed. n-hexane was found to be suitable for recovering bicyclic aromatic components in extract phase. It was suggested that the mixture of liquid aromatic components (carbon number is less than 11) could be used as re-extraction solvent. The effect of operation factors on recovering naphthalene group was examined by equilibrium re-extraction using n-hexane as solvent. With

increasing S/F and operation temperature, the distribution coefficient of bicyclic aromatic components decreased smoothly. The higher the carbon number, the higher the distribution coefficient between bicyclic aromatic, components.

3. The processes of separation and recovery for dimethylnaphthalene (DMNA) mixture with 10 structural isomers in LCO, which were composed of the extraction column for aromatic group in LCO, the re-extraction column for aromatic group in extract phase and the distillation towers for recovery of DMNAs in aromatic group mixture, could be planned using the experiment result of equilibrium extraction of the previous work and that of the equilibrium re-extraction of this work.

NOMENCLATURE

E	mass in extract phase obtained by equilibrium extraction or re-extraction (kg)
m	distribution coefficient defined by Eq. (1)(−)
R	mass in raffinate phase for equilibrium extraction or re-extraction (kg)
x	mass fraction in raffinate phase obtained by equilibrium extraction or re-extraction (−)
Y	yield defined by Eq. (2) (−)
y	mass fraction in extract phase obtained by equilibrium extraction or re-extraction (−)
Greek	
β	selectivity defined by Eq. (3) (−)
Subscript	
0	at initial ($t = 0$)
i	component *i*
j	component *j*
w	water

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