Separation of Absorption Oil by Solvent Extraction
-Separation of Extracted/Solvent Components by Distillation-

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Introduction

Absorption oil (AO), one of the coal tar fractions (b.p.=470~550 K), contains nitrogen heterocyclic compounds, such as quinoline, homocyclic compounds, such as methylnaphthalene, etc., which are useful as industrial raw materials. Currently, this AO is, firstly, separated into acid, base, and neutral fractions by reactive extraction with acid and base and these three fractions are, secondly, provided to downstream step to be separated into respective compounds. In this first separation step, there are some problems such as difficulty in solvent recovery and equipment corrosion. As an alternative to this technique, conventional solvent extraction without reaction[1]~[6] and so on are proposed. Solvent extraction separates AO into nitrogen compound and the other compounds mainly on the basis of polarity difference. In one of these studies, distillation was applied to separating extract phase into extracted and solvent components. This study showed that not only extract phase was favorably separated, but also further separation between nitrogen compound and the others could occur and bottom product formed immiscible extracted components rich and water rich phases, which were easily separated by decantation.

In this study, the effect of operating conditions on the distillation of extract phase from solvent extraction of AO was investigated. In the first, the equilibrium extraction of AO was carried out under several conditions. Next, the model mixture and the real extract phase from the AO extraction were separated by a simple distillation.

1.   Experimental

1.1 Equilibrium Extraction

The experimental conditions are summarized in **Table 1**. AO and aqueous solution of methanol were brought into contact and were shaken at 303K for 48 hours. The equilibrated oil and aqueous phases were split into each other by separation funnel.

1.2 Batch Simple Distillation

Table 2 shows the experimental conditions of batch simple distillation. The model mixture or extract phase obtained from the equilibrium extraction was used as feed. The model mixture is composed of quinoline, 2-methylnaphthalene, methanol, and water. Distillation was carried out in 1×10^{-4} m³ round bottom flask heated with an electric heating mantle and ribbon, and Graham condenser. The heating ribbon was used to prevent the internal reflux. After the first condensed distillate was obtained, the distillate was sampled every 0.05 hour. The temperature of the liquid

phase remaining in the still was measured by a digital thermometer.

1.3 Analysis

The liquid phases were analyzed using a gas chromatograph (GC2010) and a Karl Fischer's titrator (758 KFD titirino) to determine the compositions.

2.   Results and Discussion

The compositions of AO are shown in **Table 3**.Although all of the components given in **Table 3** were identified, only quinoline as a representative of nitrogen compound, 2-methylnaphthalene as a representative of homocyclic compound, methanol, and water were discussed, here, on account of limited space.

2.1   Equilibrium Extraction

The composition of extract phase, $y_{i,1}$, are shown in **Table 3**. The fractional yield of component i, $Y_{i,E}$, was defined as,

$$Y_{i,E}=(E_1 \cdot y_{i,1})/(R_0 \cdot x_{i,0}) \tag{1}$$

Figure 1 shows the relation between $Y_{i,E}$ and the mass fraction of water in solvent phase, $y_{W,0}$. The $Y_{Q,E}$ was higher than that of 2-methylnaphthalene. The water in the solvent phase lowered $Y_{i,E}$. These results were in agreement with the previous ones[7].

2.2   Batch Simple Distillation

The model extract phase and the real extract phase from the above equilibrium extraction shown in **Table 3** were used as feeds for the distillation. The composition of the model extract phase was determined according to the real extract phase and the mass fractions of quinoline and 2-methylnaphthalene in the model extract phase were fixed at almost equivalent with each other.

2.2-1 Observation of Distillation

In the cases of model extract phases and Real 3, there was only single liquid phase in the still, since the content of quinoline in the feed for the distillation was relatively low. When Real 1 and 2 were used as feeds, the still liquids consisted of two immiscible liquid phases at higher temperature: a smaller dark brown and transparent phase; and a larger colorless and transparent phase. The brown phase was rich in extracted components and the colorless phase was rich in water.

The fractional recovery, D/F, is shown in **Fig.2**. The results with Real 2 were in agreement with the previous ones[7]. The profiles of fractional recoveries were shifted to higher temperatures at higher mass fraction of water in the feed. There were no differences in D/F between the model extract phases and real extract phases.

2.2-2 Yields

The fractional yield of component i, $Y_{i,D}$, was defined as,

$$Y_{i,D}=(D \cdot x_{i,D})/(F \cdot x_{i,F}) \tag{2}$$

The yields of quinoline, 2-metylnaphthalene, methanol, and

water were shown in **Figs.3~6**. In all the runs, distillates were rich in 2-methylnaphthalene and methanol and still liquids, in quinoline and water. If bottom product consists of two immiscible liquid phases, extracted and solvent components can be separated and the further separation between quinoline and 2-methylnaphthalene could be achieved. Otherwise, other separation method such as back extraction method is required for the separation between extracted and solvent component. This phenomenon in this distillation was contrary to the boiling point order of these components given in **Table 3**. This resulted from complicated nonideality of this multi component system. The yield profiles of all the components were shifted to higher temperatures with an increase in mass fraction of water in the feed. The results for the model extract phases and the real extract phases agreed except for quinoline and 2-methylnaphthalene in the cases of Mod 1 and Real 1. At higher temperature, $Y_{Q,D}$ and $Y_{2MN,D}$ in the case of Real 1 were lower than those in the other cases, probably because Ext 1 contained large amount of quinoline which has an affinity with 2-methylnaphthalene.

3. Conclusion

The extract phase in equilibrium extraction could be separated between extracted and solvent components by distillation. In this distillation, further separation between quinoline and 2-methylnaphthalene was also carried out. On the other hand, the bottom product was homogeneous in some cases. In such a case, other separation method is required.

Nomenclature

D	:	mass of distillate in distillation	[kg]
E	:	mass of extract phase in equilibrium extraction	[kg]
F	:	mass of feed in distillation	[kg]
R	:	mass of raffinate phase in equilibrium extraction	[kg]
x	:	mass fraction in the raffinate phase	[−]
y	:	mass fraction in the extract phase	[−]
Y	:	yield	[−]

\<subscript\>

0	:	at initial state in equilibrium extraction
1	:	at equilibrium state in equilibrium extraction
D	:	distillate in distillation
F	:	feed in distillation
i	:	component i

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Table 1 Experimental Conditions for Equilibrium Extraction

Feed		AO (absorption oil)
Mass, R_0	[kg]	0.05 - 0.15
Solvent		aqueous solution of methanol
Mass fraction of water, $y_{w,0}$	[-]	0.3 - 0.7
Mass ratio of solvent to feed, E_0/R_0	[-]	1
Shaking time	[h]	48
Amplitude of shaking	[m]	0.004
Frequency of shaking	[h^{-1}]	5400
Extraction temperature	[K]	303

Table 2 Experimental Conditions for Bacth Simple Distillation

Feed	model extract phase (Q-2MN-M-W)
	or
	real extract phase from equilibrium extraction
Mass, F [kg]	0.05-0.06
Initial temperature	room temperature

Table 3 Boiling point and mass fraction

|	Boiling point [K]	mass fracton [-]						
		AO	Real extract phase			Model extract phase		
			Real 1	Real 2	Real 3	Mod 1	Mod 2	Mod 3
Quinoline	511	0.072	0.02369	0.01047	0.00278	0.00629	0.00075	0.00004
Isoquinoline	515	0.018	0.00566	0.00246	0.00063	0	0	0
Indole	526	0.035	0.00876	0.00253	0.00050	0	0	0
Naphthalene	491	0.03	0.00155	0.00023	0.00001	0	0	0
1-Methylnaphthalene	514	0.1	0.00334	0.00044	0.00003	0	0	0
2-Methylnaphthalene	514	0.243	0.00773	0.00084	0.00003	0.00598	0.00073	0.00003
Biphenyl	528	0.063	0.00215	0.00032	0.00003	0	0	0
Dibenzofuran	560	0.103	0.00281	0.00031	0.00002	0	0	0
Methanol	337	0	0.65783	0.53511	0.31474	0.72963	0.54171	0.30647
Water	373	0	0.29136	0.44239	0.69658	0.25810	0.46025	0.69347
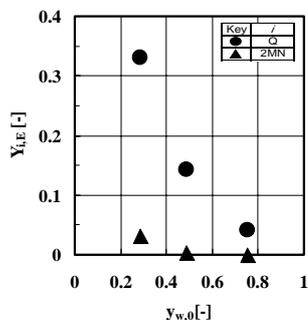
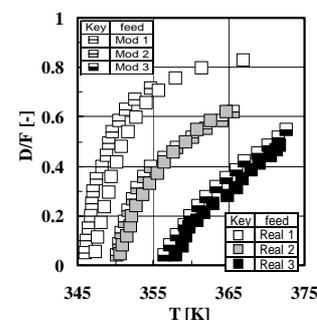**Fig.1** Yield in equilibrium extraction, $Y_{i,E}$
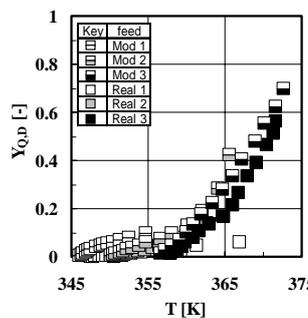

Fig. 2 Fractional Recovery, D/F

Fig.3 Yield of quinoline in distillate, $Y_{Q,D}$

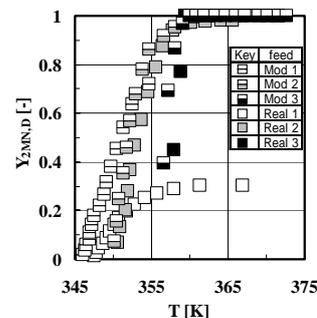**Fig.4** Yield of 2-metylnaphthalene in distillate, $Y_{2MN,D}$

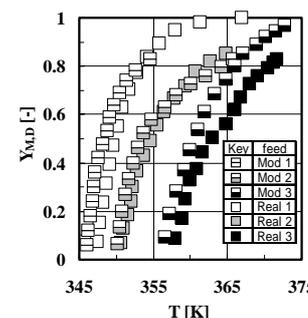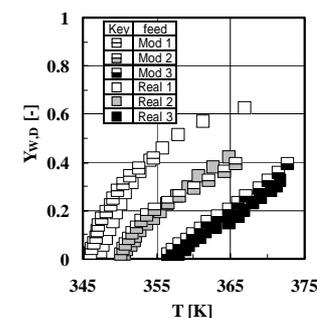**Fig.5** Yield of methanol in distillate, $Y_{M,D}$

Fig.6 Yield of water in distillate, $Y_{W,D}$