

Process of absorption oil separation using solvent extraction and distillation

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溶媒抽出法、蒸留法を用いたコールタール吸収油の分離プロセス

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まず、吸収油に含まれる成分の一部(キノリン, 2-メチルナフタレン)および抽出溶媒成分(メタノール, 水)からなるモデル系に対して、計算により気液液平衡関係を推定した。ついで、吸収油の溶媒抽出における抽出相を想定した同モデル混合物の回分単蒸留を行い、前述の推定結果を定性的に確認した。さらに、これらの結果およびプロセス計算に基づいて、吸収油を窒素素複素環式化合物と同素環化合物等とに分離するプロセスを合成、提案した。

1. Introduction

Absorption oil (AO), one of the coal tar fractions (b.p. =470~550K), contains nitrogen heterocyclic compounds, such as quinoline (Q), homocyclic compounds, such as 2-methylnaphthalene (2MN), 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. To solve these problems, several alternative methods, such as solvent extraction method, have been studied. Solvent extraction technique can separate AO into nitrogen compound and the other compounds by polarity difference. In one of these studies^[1], distillation was applied to recover the extraction solvent, mixture of methanol(M) and water (W). In this distillation, the bottom product formed two immiscible liquid phases; extracted components rich and water rich phases. These were easily separated by decantation. As result, this study showed that not only recovery of solvent, but also further separation between nitrogen compound and the others were achieved.

In this study, the AO separation process including the solvent recovery was investigated. In the first, the phase equilibrium of representative components of AO and solvent components was calculated. Next, the mixture of AO and solvent components were separated by a simple distillation. Finally, some AO separation processes were investigated by calculation.

2. Phase equilibrium in AO and solvent components

2.1. Calculation

The mass fraction of some main compounds in AO is shown in **Table 1**. Q and 2MN are largest components in nitrogen heterocyclic compounds and homocyclic compounds in AO, so these were selected as representative components. Phase equilibrium in Q-2MN-M-W quaternary system was calculated. In this calculation, following equations were used,

< Thermodynamic equation >

$$y_i P = \gamma_i^A x_i^A P_i^S = \gamma_i^B x_i^B P_i^S \quad (i = 1, 2, \dots, C) \quad (1)$$

< Material balance equation >

$$F = V + L^A + L^B \quad (2)$$

$$Fz_i = Vy_i + L^A x_i^A + L^B x_i^B \quad (i = 1, 2, \dots, C) \quad (3)$$

where x_i , y_i , P and P_i^S denote the mole fraction of

component i in liquid phase, that in vapor phase, the total pressure and saturated vapor pressure of component i . Thermodynamic equations consist of two parts: vapor - liquid equilibrium part and liquid - liquid equilibrium part, and overall equation shows vapor - liquid - liquid equilibrium. The UNIFAC thermodynamic model and Antoine equation were applied estimating the activity coefficient, γ_i , and saturated vapor pressure of component i , P_i^S .

Table 1 Mass fraction of component i in AO

Nitrogen heterocyclic compounds			Homocyclic hydrocarbons etc.				
Q	IQ	IL	N	1MN	2MN	BP	DBF
0.07	0.02	0.04	0.03	0.10	0.24	0.06	0.10

2.2. Result

2.2.1 Liquid-liquid equilibrium

The two liquid phases region in quaternary system is shown in **Fig.1**. For example, solvent extraction calculation was carried out with the conditions in **Table 2**, and extract phases on tieline were obtained. **Table 3** shows composition of feed, solvent, and extract phase.

Table 2 Calculation conditions for solvent extraction

Feed	model AO
Solvent	three type of methanol aqueous solution
Mass ratio of solvent to feed, S/F	1
Pressure, P	1 [atm]
Temperature, T	293 [K]

Table 3 Composition of feed, solvent and extract phase

	feed	solvent			extract phase		
		solA	solB	solC	extA	extB	extC
Q	0.197	—	—	—	0.0181	0.040	0.06
2MN	0.803	—	—	—	0.0003	0.003	0.02
M	—	0.3	0.5	0.7	0.2635	0.442	0.61
W	—	0.7	0.5	0.3	0.7181	0.515	0.31

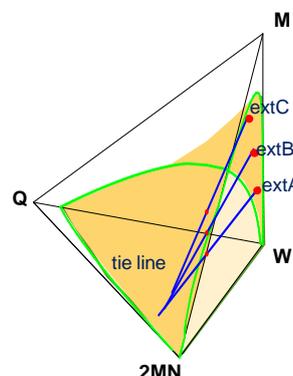


Fig.1 Phase diagrams at 293K and 1atm

2.2.2 Vapor-liquid and vapor-liquid-liquid equilibrium

Vapor-liquid and vapor-liquid-liquid equilibrium are

difficult to present in tetrahedral coordinate like **Fig.1**, so that it is discussed by using **Fig.2**. These graphs show effect of temperature on phase equilibrium, and average compositions in each graph were fixed in the composition of extA, extB and extC. In the figure, result of only Q and W are shown. When temperature was lower than boiling point, there was one liquid phase. In area b, there were vapor and liquid phases. In all case, liquid phase was water phase. In area c, there were one vapor and two liquid phases. In the case of when water content was relatively high such as extA, this three phases region was narrow. In area d, there were vapor liquid and liquid phases. In the case of extA, liquid phase was water phase. On the other hand, In the cases of extB and extC, liquid phase was oil phase. In area e, there is one vapor phase.

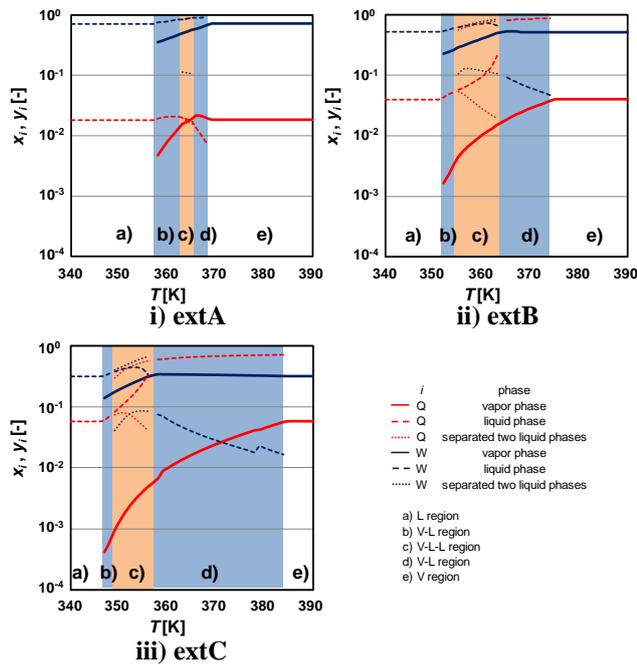


Fig.2 Effect of temperature on phase equilibrium

3. Batch simple distillation of AO and solvent mixture

3.1. Experimental

The experimental conditions are shown in **Table 4**. The real extract phase and model extract phase and were used as feeds for the distillation. The composition of these feeds are shown in **Table 5**. The data of RunNo1~6 were from previous study^[2].

3.2. Result

The still liquids consisted of two immiscible liquid

Mass, F	[kg]	0.05-0.06
Sampling interval	[min]	3
Distillation time	[min]	45
Initial temperature	[K]	room temperature

Run No	1	2	3	4	5	6	7	8	9	10	11
	real	real	real	model	model	model	model	model	model	model	model
Q	0.0237	0.0105	0.00278	0.006	0.0007	0.00004	0.006	0	0.007	0.022	0.042
IQ	0.0057	0.0025	0.00063	—	—	—	—	—	—	—	—
IL	0.0088	0.0025	0.00050	—	—	—	—	—	—	—	—
N	0.0015	0.0002	0.00001	—	—	—	—	—	—	—	—
1MN	0.0033	0.0004	0.00003	—	—	—	—	—	—	—	—
2MN	0.0077	0.0008	0.00003	0.006	0.0007	0.00003	0	0.006	0.003	0.007	0
BP	0.0022	0.0003	0.00003	—	—	—	—	—	—	—	—
DBF	0.0028	0.0003	0.00002	—	—	—	—	—	—	—	—
M	0.658	0.535	0.315	0.730	0.5417	0.30647	0.664	0.664	0.654	0.655	0.641
W	0.291	0.442	0.697	0.258	0.4568	0.69347	0.330	0.331	0.336	0.316	0.317

phases at higher temperature in the cases of RunNo1, 2, 10, and 11. In this run, the content of Q in the feed for the distillation was relatively high.

Figure 3 shows mass fraction in each phase in RunNo6 and 10. In these graph, effect of temperature on phase equilibrium that average composition fixed in extA and extC are shown also. Feed in RunNo6 and extA had near water and methanol content, and feed in RunNo10 and extC had near water and methanol content. If compare the change of mass fraction with increment of temperature in RunNo6 with phase equilibrium, they had same tendency of increment. But the orders of mass fraction of Q in RunNo6 were different from that in the case of extA, and it was due to difference of feed composition. As result, phase equilibrium by calculation was confirmed qualitatively.

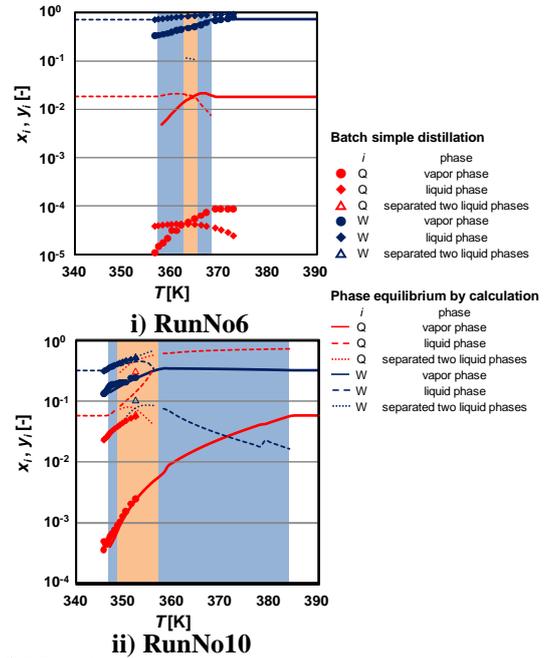


Fig.3 Mass fraction of component *i* in each phase

Based on these results, two flows for solvent recovery were proposed (**Fig.4**). One is that bottom product consist one liquid phase. Solvent components are recovered as top product, and bottom product become nitrogen heterocyclic compounds product. But when water content in extract phase is high, this flow can't be applied because bottom product becomes pure water. The other is that bottom product is separated into aqueous phase and organic phase. Solvent components are recovered as the mixture of top product and aqueous phase. Organic phase become nitrogen compounds product.

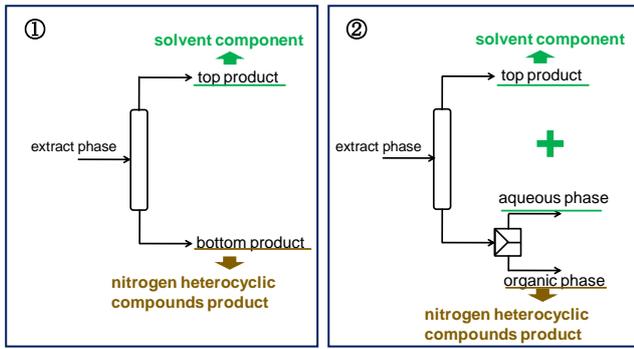


Fig.4 Schematic diagram of flow for solvent recovery

4. Process of AO separation

4.1 Process scheme

The schematic flow sheet of AO separation process is shown in Fig.5. The AO is separated roughly into nitrogen heterocyclic compounds and other compounds by using solvent extraction with methanol aqueous solution. Single-stage extraction was applied. Next, the solvent components in extract phase are recovered by distillation and nitrogen heterocyclic compounds product is obtained. For this distillation, multi-stage distillation was applied.

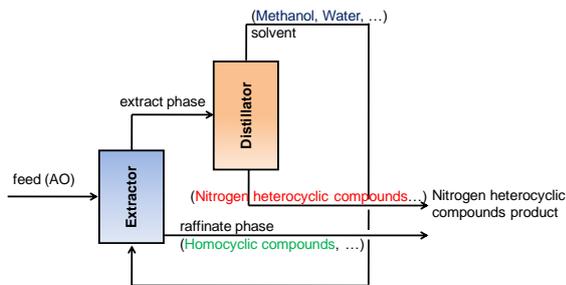


Fig.5 Schematic diagram of AO separation process

4.2 Calculation

4.2.-1 Solvent extraction

Single-stage extraction was carried out with same conditions in chapter 2 (Table 2), and extA, extB and extC were used as feed of following distillation.

4.2.-2 Distillation

This calculation was conducted by the commercial process simulator CHEMCAD III. Table 6 shows the calculation conditions of the distillation. Thermodynamic model was same as that in previous chapter. The conditions and specifications of distillation calculation are summarized in Table 7. According to the process suggestions in chapter3, three kinds of cases were examined.

Table 6 Calculation conditions of distillation

Number of stages	15
Condenser	total condenser
Extract phase flow rate, F	[kg] 1
Pressure, P	[atm] 1
Feed	liquid at boiling point
Feed stage, n_F	$\min T_F - T_{n_F} $

Table 7 Specifications in each Case

	Spec 1	Spec 2
Case1	$D = Fz_M$	$Wx_M < 1 \times 10^{-4}$
Case2	$D = Fz_M + Fz_W$	reflux ratio, $R = 1$
Case3	$Wx_W < 1 \times 10^{-4}$	reflux ratio, $R = 1$

4.3 Result

The results are shown in Table 8. In RunNoA2 and A3,

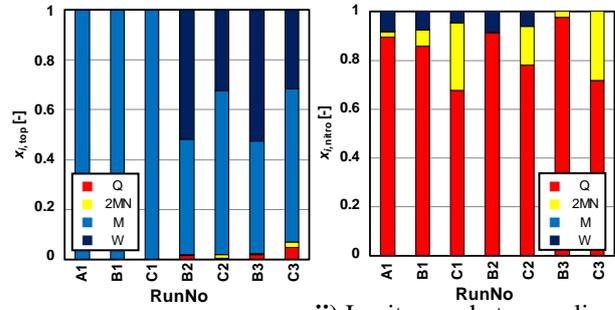
solvent recovery was not achieved. In RunNoA2, bottom product became pure water as expected, and A3, specification could not be satisfied. In Case1 or 2, solvent recovery was achieved by flow ②. On the other hand, in Case3, that was achieved by flow ①.

Table 8 Result of each RunNo

RunNo	Case	ext	Solvent recovery
A1	1	A	②
B1	1	B	②
C1	1	C	②
A2	2	A	×
B2	2	B	②
C2	2	C	②
A3	3	A	×
B3	3	B	①
C3	3	C	①

Mass fraction

Figure 6 shows the mass fractions in top product and nitrogen compounds product. In Case3, water was not contained in the nitrogen heterocyclic compounds product. On the other hand, when applied Case1 or 2, it is inevitable that water was contained in the nitrogen compounds product with amount of solubility. The products that extracted component content was over 90% were obtained.



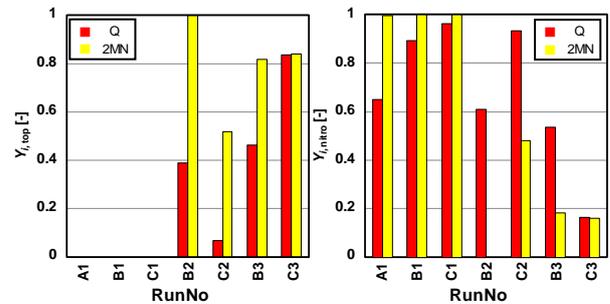
i) In top product, $x_{i,top}$

ii) In nitrogen heterocyclic compounds product, $x_{i,nitro}$

Fig.6 Mass fraction of component i in top product and nitrogen heterocyclic compounds product

Yield

Figure 7 shows the yield in top product and nitrogen compounds product. In Case1, $Y_{2MN,nitro}$ was larger than $Y_{Q,nitro}$. It is due to small solubility of 2MN in the aqueous phase. On the other hand, in Case2 or 3, $Y_{Q,nitro}$ was larger than $Y_{2MN,nitro}$ because 2MN was contained in top product. Further separation between nitrogen compounds and the others was occurred.



i) In top product, $Y_{i,top}$

ii) In nitrogen heterocyclic compounds product, $Y_{i,nitro}$

Fig.7 Yield of component i in top product and nitrogen heterocyclic compounds product

Energy requirement (reboiler duty)

Figure 8 shows the energy requirement that is equal to reboiler duty in the each run. The energy requirement in Case3 was higher than that in Case1 or 2. In addition, the range of distillation temperature in Case3 was very wide. In Case1 and 2, the highest temperature in the column was about 372K, but that in Case3 was about 510K.

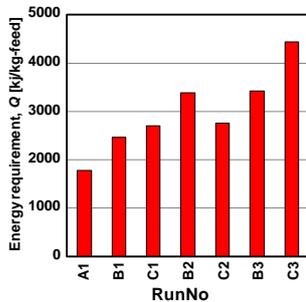


Fig.8 Energy requirement, Q

When water content in extract phase is low such as extC, Case2 shows high purity, further separation between Q and 2MN and low energy requirement. When water content in extract phase is high such as extA, it is necessary to select Case1 because bottom product became pure water so solvent recovery can't be achieved in Case2 or 3.

4. Conclusions

First, by calculation of phase equilibrium, it was confirmed that when water content in feed was high vapor-liquid-liquid three phases region was small and liquid phase was water at high temperature. On the other hand, when water content was low, liquid phase was oil. Next, by batch simple distillation, phase equilibrium by calculation was confirmed qualitatively. Based on the result of phase equilibrium estimation and batch simple distillation, two type of solvent recovery were proposed. Finally, process of AO separation was estimated and accessed, and AO separation and solvent recovery were achieved.

Acknowledgment

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Nomenclatures

C	= number of components	[-]
D	= mass of distillate	[kg]
E	= mass of extract phase	[kg]
F	= mass of feed	[kg]
L	= mole of liquid phase	[mol]
Q	= energy requirement	[kJ/kg-feed]
R	= reflux ratio	[-]
S	= mass of extraction solvent	[kg]
V	= mole of vapor phase	[mol]
W	= mass of bottom product	[kg]
x	= mole or mass fraction in liquid phase	[-]
y	= mole or mass fraction in vapor phase	[-]
z	= mole or mass fraction in feed	[-]
Y	= yield	

<Greek>

γ	= activity coefficient	[-]
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<Subscript>

1MN = 1-methylnaphthalene

2MN = 2-methylnaphthalene

AO = absorption oil

BP = biphenyl

D = distillate

DBF = dibenzofuran

E = extraction solvent

F = feed

i = component i

IL = indole

IQ = isoquinoline

N = naphthalene

nitro = nitrogen heterocyclic compounds product

Q = quinoline

top = top product

<Superscript>

A = liquid phase A

B = liquid phase B

S = saturated vapor

Literature Cited

- [1] Salim, C, Egashira, R; *Journal of the Japan Petroleum Institute*, **49**, (6), 326 (2006)
- [2] Yoshimura, Y; Bachelor thesis, Tokyo Tech (2008)