

# ROUGH SEPARATION PROCESS OF COAL TAR ABSORPTION OIL USING SOLVENT EXTRACTION METHOD

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## 溶媒抽出法を用いたコールタール吸収油の粗分離プロセス

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まず、メタノール水溶液を溶媒としてコールタール吸収油中の含窒素複素環式化合物 Ar-N を平衡抽出した。得られた抽出相は、単蒸留あるいは第 2 の溶媒 (トルエンなど) との接触 (逆抽出、平衡) により、Ar-N を主な成分とする抽出物に富んだ留分と溶媒成分 (メタノールおよび水) に富んだ留分とに分離 (溶媒回収) できた。ついで、これらの実験結果に基づいて還流を伴う向流多段抽出プロセスの計算を行った。蒸留法あるいは逆抽出と蒸留を組み合わせた方法のいずれによっても溶媒回収は可能であり、本プロセス全体としてコールタール吸収油の粗分離、すなわち Ar-N とその他の成分 (同素環式化合物、含酸素複素環式化合物、等) との分離が可能であることを示した。

## 1. Introduction

Coal tar (tar), one of the products from coal carbonization, contains many useful compounds to chemical industry. Generally these compounds are separated from distilled tar fractions. One of the fractions, absorption oil fraction (AO), b.p. 470~550K, contains homocyclic hydrocarbons (HC) such as 1-methylnaphthalene (1MN), 2-methyl-naphthalene (2MN), biphenyl (BP), etc, heterocyclic nitrogen compounds (Ar-N) such as quinoline (Q), isoquinoline (IQ), indole (I), etc, heterocyclic oxygen compounds (Ar-O) such as dibenzofuran (DBF), etc. These compounds can be used to produce insecticides, coloring matters, medicine, dyes, etc.

Industrially, the separation and purification of these compounds from AO include ① acidic and basic extractions which separate these compounds into three streams of acidic and basic compounds with high polarity, and low polarity compounds and ② purification of each streams using distillation, crystallization, adsorption, etc. However acidic and basic extractions have some difficulties concerning corrosion of extraction vessels, solvent recovery, etc which cover a large part of the operational cost. Therefore a more efficient and easier way to separate AO is needed.

Methods for separating Ar-N and HC from the coal tar absorption oil or similar mixture oils have been studied.

Nagai et al. compared two kinds of solvent (aqueous methanol and sulfolane) in extracting nitrogen compounds from absorption oil<sup>1)</sup>.

The author showed that addition of metal ion in the methanol (aq) solvent can increase the efficiency of separating quinolines from absorption oil<sup>2)</sup>.

The purpose of this study is to evaluate the feasibility of a rough separation process in separating Ar-N from HC and Ar-O in coal tar absorption oil.

## 2. Equilibrium Extraction of Coal Tar Absorption Oil (ME)

The separation of Ar-N from HC and Ar-O in AO can be done effectively using methanol (aq) as solvent as suggested in previous study<sup>1)2)</sup>.

Conditions for equilibrium extraction of AO (ME) is shown in Table 2.1. Feed  $R_0$  and solvent  $E_0$  were contacted at 303K and separated into extract phase  $E_1$  (solvent-rich phase) and raffinate  $R_1$  after the extraction. These phases were analyzed using gas chromatograph (for determining methanol M, Q, IQ, I, 2MN, 1MN, BP, DBF) and Karl Fischer (for determining water W contents in AO and  $R_1$ ).

Table 2.1 Conditions in ME

Feed $R_0$	: absorption oil (AO) 20~40g;
Solvent $E_0$	: aqueous methanol;
$E_0/R_0 = 1\sim 4$ ;	Water concentration in $E_0$ $y_{0,W} = 0.3\sim 0.7$ ;
Extraction Temperature	: 303K
$x_{0,Q} = 0.088$ ; $x_{0,IQ} = 0.024$ ; $x_{0,I} = 0.052$ ; $x_{0,2MN} = 0.28$	
$x_{0,1MN} = 0.12$ ; $x_{0,BP} = 0.081$ ; $x_{0,DBF} = 0.062$	

Distribution coefficient of components  $m_{1,i}$ , which was defined as ratio of component's concentration in  $E_1$  ( $y_{1,i}$ ) and in  $R_1$  ( $x_{1,i}$ ), yield of components in extract  $Y_{1,i}$  (ratio of component's mass in  $E_1$  and  $R_0$ ), and separation selectivity of components compared to 2MN  $\beta_{i,2MN}$  (ratio of  $m_{1,i}$  to  $m_{1,2MN}$ ) were used to evaluate separation efficiency in ME

$$m_{1,i} = y_{1,i}/x_{1,i} \quad (2.1) \quad Y_{1,i} = (E_1 y_{1,i}) / (R_0 x_{0,i}) \quad (2.2)$$

$$\beta_{i,2MN} = m_{1,i} / m_{1,2MN} \quad (2.3)$$

Table 2.2 shows  $y_{1,i}$  from one of the results. It shows that Ar-N concentrated in extract compared to AO.

Table 2.2 Composition in  $E_1$  ( $y_{0,W} = 0.3$ ,  $E_0/R_0 = 2$ )

$y_{1,M} = 0.598$ ; $y_{1,W} = 0.290$
$y_{1,Q} = 0.022$ ; $y_{1,IQ} = 0.006$ ; $y_{1,I} = 0.011$ ; $y_{1,2MN} = 0.10$
$y_{1,1MN} = 0.005$ ; $y_{1,BP} = 0.003$ ; $y_{1,DBF} = 0.002$

The effect of water concentration in extract  $y_{1,W}$  on  $y_{1,i}$ ,  $m_{1,i}$ ,  $\beta_{i,2MN}$  and  $Y_{1,i}$  are shown in Fig.2.1 to 2.4.

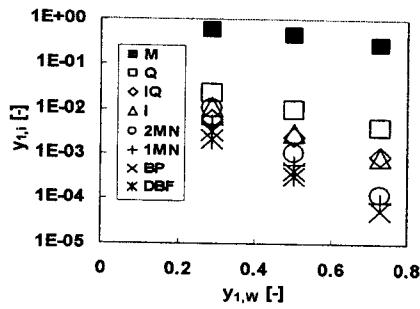


Figure 2.1 Effect of water conc. on components concentration in extract

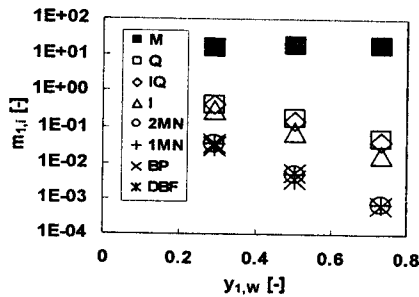


Figure 2.2 Effect of water conc. in extract on distribution coefficient of components

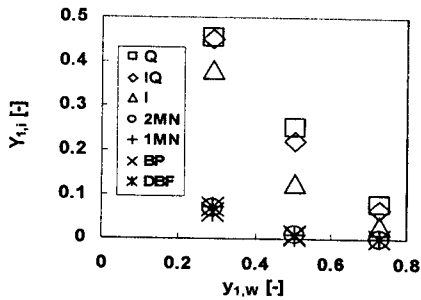


Figure 2.3 Effect of water conc. on yield of components in extract

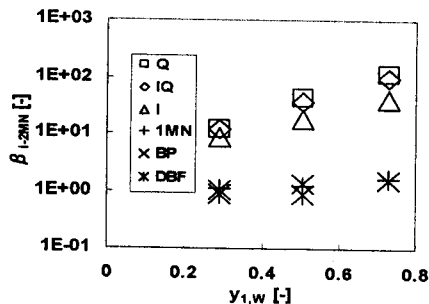


Figure 2.4 Effect of water conc. in extract on separation selectivity of components compared to 2MN

In all the results, those of Ar-N are higher than those of HC and Ar-O which means that Ar-N was separated from HC and Ar-O.  $m_{1,i}$  and  $Y_{1,i}$  of components decreased with the increase of  $y_{1,w}$ . However the selectivity of Ar-N to 2MN  $\beta_{i-2MN}$  increased and reached about 100 in the condition

$y_{1,w}=0.7$ . Comparison of measured equilibrium in this study and those of previous studies<sup>12)</sup> has shown similar results.

### 3. Solvent Recovery by Distillation

Simple distillation was done to recover methanol (aq) from extract of ME ( $E_1$ ).

Yield of component in distillate  $Y_{D,i}$  was defined as ratio of component's mass in distillate  $E_{3T}$  and feed  $E_2$ .  
 $Y_{D,i} = (E_{3T}y_{3T,i}) / (E_2y_{2,i})$  (3.1)

Distillate  $E_{3T}$  from top was rich in M and liquid left in the bottom separated into aqueous phase  $E_{3B}$  and oil phase  $E_4$ , which contains Ar-N, HC and Ar-O.

Methanol was concentrated in  $E_{3T}$  with concentration in  $E_{3T}$   $y_{3T,M}$  about 0.7 and the extractant's (Q, IQ, I, 2MN, 1MN, BP, DBF)  $y_{3T,i}$  reached only 0.008 in the result shown in Fig.3.1.

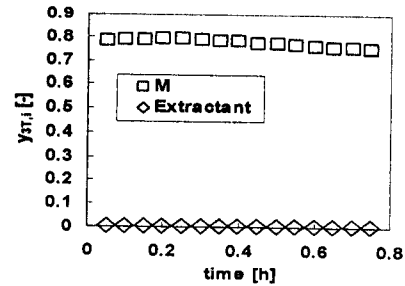


Figure 3.1 The change of distillate composition with the passage of time

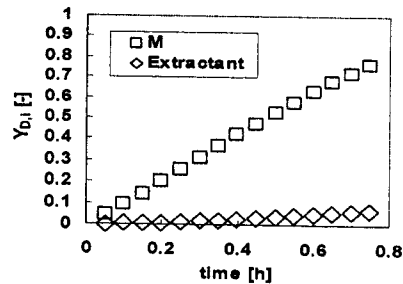


Figure 3.2 The change of yield of components in distillate with the passage of time

$Y_{D,i}$  of M and extractant increased with the passage of time and reached about 0.78 and 0.07 respectively as shown in Fig.3.2.

Although the separation of M using simple distillation can be done, it is not efficient enough for a real process. Therefore a better distillation method such as rectification can be used to achieve a better separation and recovery of M from  $E_2$  (higher  $y_{3T,M}$ ,  $Y_{D,M}$ ; lower  $y_{3T,extractant}$ ,  $Y_{D,extractant}$ ).

#### 4. Solvent Recovery by Equilibrium Extraction (RE)

The conditions for equilibrium extraction of  $E_1$  (extract from ME) is shown in Table 4.1. Feed  $E_2$  ( $E_2=E_1$ ) and solvent  $R_2$  was contacted at 303K and then separated into aqueous phase  $E_3$  and oil phase  $R_3$ .

Table 4.1 Conditions in RE

Feed $E_2$	: extract from ME $E_1$ 20g;
Solvent $R_2$	: heptane H or toluene T;
$R_2/E_2 = 1-4$ ; Extraction Temp.	: 303K

Distribution coefficient of components in RE  $m_{2,i}$  was defined as ratio of component's concentration in  $E_3$  ( $y_{3,i}$ ) and oil phase  $R_3$  ( $x_{3,i}$ ). And yield of components in  $R_3$   $Y_{2,i}$  was defined as ratio of component's mass in  $R_3$  and  $E_2$ .

$$m_{2,i} = y_{3,i}/x_{3,i} \quad (4.1) \quad Y_{2,i} = (R_3 x_{3,i}) / (E_2 y_{2,i}) \quad (4.2)$$

By contacting T or H with  $E_1$ , extractants (Q, IQ, I, 2MN, 1MN, BP, DBF) from  $E_1$  dissolved into T or H.

The result of  $m_{2,i}$  is shown in Fig.4.1. Extraction of  $E_2$  using T as solvent (T) resulted in a lower  $m_{2,i}$  than of that using H as solvent (H). The values of  $m_{2,i}$  (T) were close to  $m_{1,i}$  while that of (H) were higher. This shows that RE using T as solvent was more efficient than that using H in recovering methanol (aq).

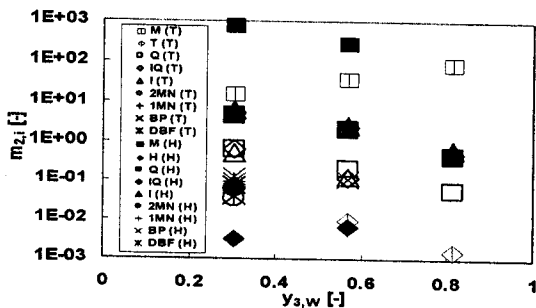


Figure 4.2 Effect of water concentration in  $R_3$  on distribution coefficients of components

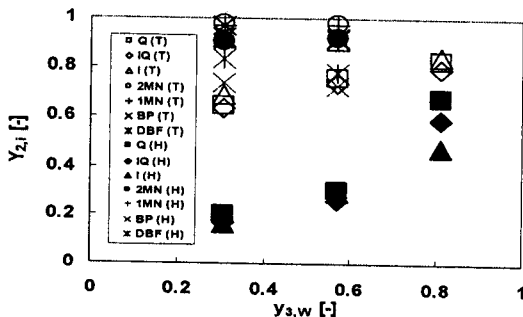


Figure 4.3 Effect of water concentration in  $R_3$  on yield of components in extract of RE

The increase in water concentration in  $E_3$  ( $y_{3,w}$ ) resulted in the decrease of  $m_{2,i}$  (Fig.4.1) and the

increase of  $Y_{2,i}$  of components in  $R_3$  (Fig.4.2) which means that the extraction efficiency in RE increase with the increase of  $y_{3,w}$ .

However, the increase in  $y_{3,w}$  (which in turn caused by the increase of  $y_{1,w}$ ) also means that less amount of extractants are extracted from AO (Fig.2.3). Hence, by changing the conditions in ME (for example  $y_{0,w}$ ,  $E_0/R_0$ ) an optimum result in separation of AO and recovery of methanol (aq) can be obtained.

#### 5. Rough Separation Process of Absorption Oil

Diagram of the process is shown in Fig.5.1. AO feed F is introduced into a multistage extraction vessel and contacted with methanol (aq) solvent  $E_{n+1}$ . The extract phase  $E_1$  come out at top of the vessel while raffinate phase  $R_n$  come out from bottom of the vessel.  $E_1$  then move into solvent recovery section where two kinds of solvent recovery, distillation (process A) or the combination of extraction and distillation (process B), will be used to recover methanol (aq) from  $E_1$ .

Process A was shown in Fig.5.2 and process B was in Fig.5.3.

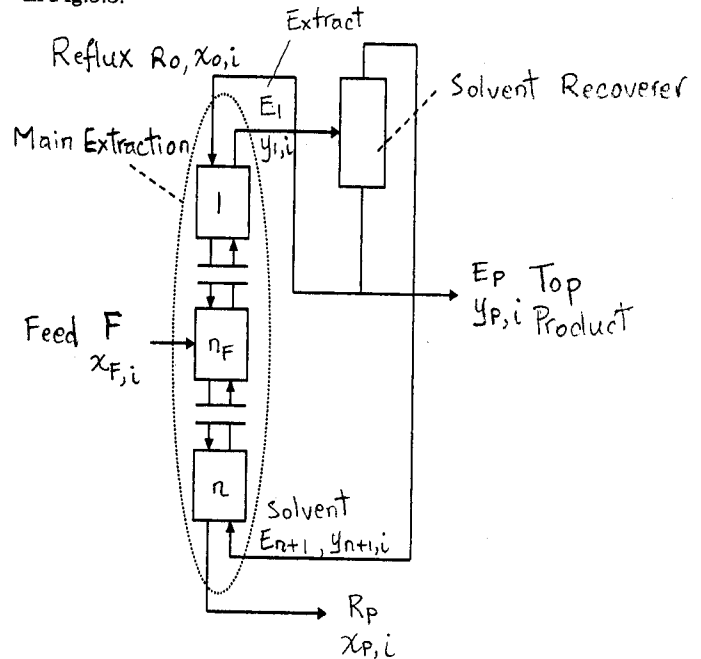


Figure 5.1 Process Flow Diagram

The equations used in this calculation of this rough separation process include material balance, liquid-liquid equilibrium (measured experimentally), mass fraction constraints and other defined equations such as reflux rate, yield, etc.

Equation solver (EQUATRAN) was used to calculate these equations and unit operation simulator (ChemCADIII) was used to calculate the energy needed in distillation.

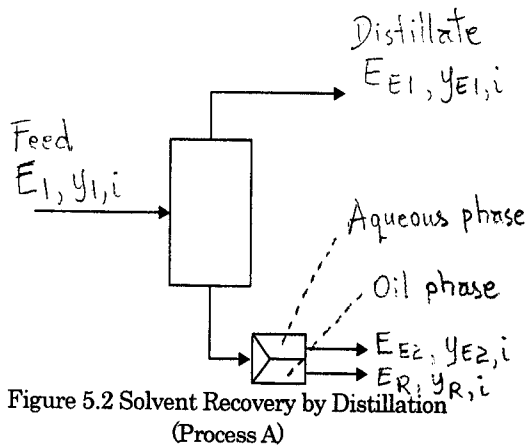


Figure 5.2 Solvent Recovery by Distillation (Process A)

The comparison of solvent recovery methods is shown in Fig.5.5. The reboiler's heat rate  $Q_R$  needed in distillation in Process A and B are compared.

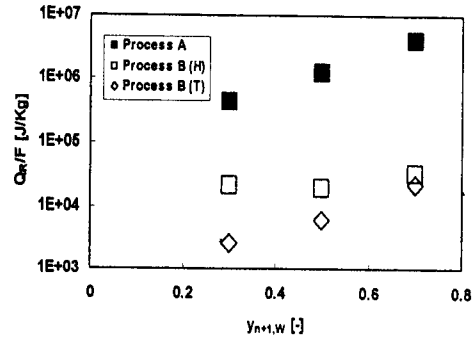


Figure 5.5 Effect of water concentration in R3 on reboiler heat duty needed in RE

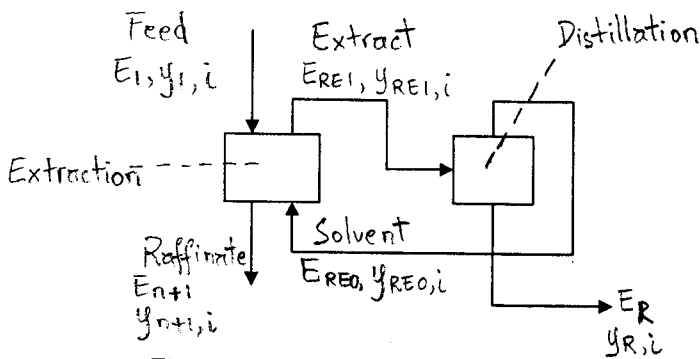


Figure 5.3 Solvent Recovery by Combination of Extraction and Distillation (Process B)

Figure 5.4 shows the effect of number of stages  $n$  in multistage extraction of AO on reflux ratio  $r$  and solvent to feed ratio  $E_{n+1}/F$  needed when the yield and concentration of Ar-N in product  $E_P$  were kept constant ( $Y_{Ar-N}=0.56$ ,  $y_{PAr-N}=0.96$ ). By increasing the number of stages  $n$  of the extraction vessel the reflux ratio  $r$  and  $E_{n+1}/F$  needed to reach the same yield and concentration of Ar-N in  $E_P$  can be decreased. The increase in  $y_{0,W}$  resulted in the decrease of  $r$  needed. However it increased the amount of solvent needed to reach the same specification.

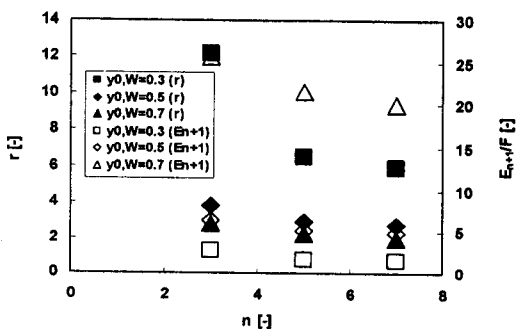


Figure 5.4 Effect of Number of Stages in Multi-Stage Extraction on Reflux Ratio and Solvent to Feed Ratio

Under this specification, the extraction of AO can be done with low enough reflux ratio and solvent to feed ratio for a real process.

The calculation of the required heat duty in distillation for Process A and B in Fig.5.5 was done under similar specification. Comparison of these processes shows that Process A required higher amount of energy than Process B. And Process B using H as solvent required higher amount of energy than Process B using T as solvent. However, there are also other factors needed to be considered in evaluating these process, for example, number of vessels or size of those needed to perform solvent recovery, or cost of solvents, etc.

## 6. Conclusion

Solvent extraction method using methanol (aq) can be used to separate components in AO.

The feasibility of distillation method and reversed-extraction method using heptane or toluene as solvent to recover methanol (aq) has been confirmed experimentally. And under the conditions of this study, RE using toluene shows a better separation efficiency than that using heptane.

Simulation of the rough separation process shows that Process B required lower energy than Process A.

The results above confirmed the feasibility of rough separation process to separate coal tar absorption oil using solvent extraction method.

### Acknowledgement

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### References

- 1) Egashira, R. and M. Nagai, Sekiyu Gakkaishi, 43, 339~345 (2000)
- 2) Egashira, R. and C. Salim, Sekiyu Gakkaishi, 44, 178~182 (2001)