

Separations of absorption oil and tar light oil by solvent extraction method

SAITO JUN

Student ID No.: 00-1010-0

Supervisor: EGASHIRA RYUICHI

Department of International Development Engineering, School of Engineering,
Tokyo Institute of Technology, Tokyo 152-8552, Japan

Introduction

Absorption oil (abbreviated to AO, b.p.=470~550 K) and tar light oil (TLO, b.p.=~440 K) are distilled from coal tar. These coal tar fractions contain various kinds of industrially useful compounds, such as nitrogen heterocyclic compounds and homocyclic aromatic compounds. The separation of the AO by solvent extraction has been studied to obtain these useful components¹⁻⁷. In these studies, Salim *et al.* separated the extractives from the extract phase by extraction with the secondary solvent, toluene and heptane, so-called re-extraction⁷.

This thesis tried the re-extraction with TLO in the extraction of AO and vice versa, namely, the simultaneous separations of AO and TLO by the solvent extraction with a single solvent. The liquid-liquid equilibria were measured under various conditions and, according to these results, the simple prototype of the process was synthesized.

1. Experimental

Specific amounts of the feed oil, R_0 , and aqueous solvent phase, E_0 , were brought into contact and were shaken at 303 K for 48 hours. The attainment to equilibrium within 48 hours was confirmed in the previous work⁴. The equilibrated oil and aqueous phases, R and E , were split into each other by separation funnel. The compositions of R_0 , E_0 , R , and E were determined by the analysis with a gas chromatograph. Karl Fischer's titration was conducted to give the water content in the oil phase. The water content in the aqueous extract phase was calculated by the material balance.

The conditions for material systems are summarized in **Table 1**. The feed oil was the AO or TLO. The aqueous solution of methanol (MeOH aq.) or the extract phase, E , equilibrated with the other feed oil was used as an aqueous phase.

2. Results and Discussion

2.1 Compositions of absorption oil and tar light oil

The gas chromatograms and compositions of AO and TLO are shown in **Fig.1** and **Table 2**, respectively. There were numbers of components in AO and TLO as found in the chromatograms. The mass fractions of the components tabulated in the table contained in AO and TLO and the solvent components, methanol (MEOH) and water (W), were determined in this study. The AO contained bicyclic compounds mainly and the TLO, monocyclic compounds.

2.2 Operation

The density of methanol is $790 \text{ kg}\cdot\text{m}^{-3}$ and those of the methanol solutions used in this study were, thus, $840 \text{ kg}\cdot\text{m}^{-3}$ to

$930 \text{ kg}\cdot\text{m}^{-3}$. In the case of AO, the phase separation could be performed easily, since the density of AO was more than $1,000 \text{ kg}\cdot\text{m}^{-3}$. On the other hand, the density of TLO was slightly less than $1,000 \text{ kg}\cdot\text{m}^{-3}$, so that the two phases could not be separated easily in some cases of TLO.

2.3 Numerical relationships

One can write the material balance relationship in terms

Table 1 Conditions of material systems

Feed	absorption oil, tar light oil		
Solvent	aqueous solution of methanol, aqueous extract phase equilibrated with the other feed oil		
	mass fraction of water, $y_{w,0}$	[-]	0.3-0.7
	mass ratio of solvent to feed, E_0/R_0	[-]	0.25-4

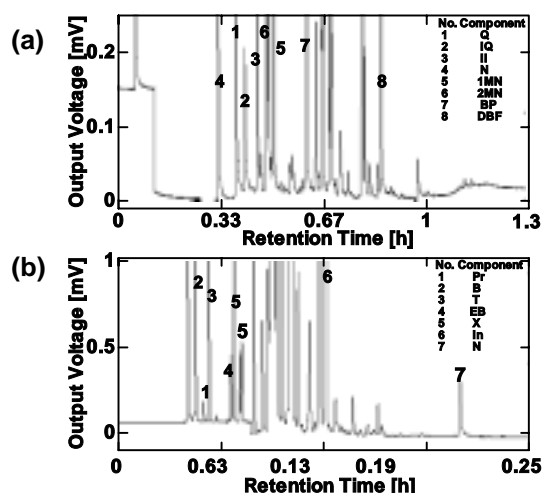


Fig.1 Gas chromatograms: (a) absorption oil; (b) tar light oil

Table 2 Mass fractions and normal boiling points of components in absorption oil and tar light oil

Component, i	Mass fraction, $x_{i,0}$ [-]		Boiling point [K]
	in AO	in TLO	
Nitrogen heterocyclic compound			
Pyridine, Pr	0	0.01	389
Quinoline, Q	0.09	0	511
Isoquinoline, IQ	0.02	0	515
Indole, Il	0.06	0	526
Homocyclic compound			
Benzene, B	0	0.25	353
Toluene, T	0	0.10	384
Ethylbenzene, EB	0	0.02	409
Xylene, X	0	0.10	412~418
Indene, In	0	0.07	456
Naphthalene, N	0.02	0.01	491
1-methylnaphthalene, 1MN	0.12	0	514
2-methylnaphthalene, 2MN	0.25	0	514
Biphenyl, BP	0.08	0	528
Oxygen heterocyclic compound			
Dibenzofuran, DBF	0.09	0	560

Received on February 19, 2004. Correspondence concerning this article should be addressed to J. Saito (E-mail address: jsaito@ide.titech.ac.jp).

of the mass changes of constituent i in respective phases with the mass fractions, $x_{i,0}$, x_i , $y_{i,0}$, y_i , as follows:

$$R_0 \cdot x_{i,0} - R \cdot x_i = (E_0 \cdot y_{i,0} - E \cdot y_i) \quad (1)$$

These relationships were almost fine for all the components except for some components whose mass transfer amounts were relatively low.

The distribution coefficient of component i , m_i , was defined by,

$$m_i = y_i / x_i \quad (2)$$

2.4 Distribution coefficient

The distribution coefficients, m_i , derived by Eq.(2) were plotted against the water content in the extract phase, y_w , for AO, TLO, toluene⁷⁾, and heptane⁷⁾ as oil phases in Fig.2(a)~(d).

The m_i s of nitrogen compounds were higher than those of aromatics in all material systems. It was confirmed that AO and TLO could be separated by the extraction with an aqueous methanol solution. The m_i s decreased in the order of pyridine, quinolines and indole, monocyclic aromatics, and bicyclic aromatics and dibenzofuran. The water in the extract phase lowered m_i s, except for m_{MeOH} . The m_i s in the cases of AO, TLO, and toluene were almost equivalent to one another and were lower than that in the case of heptane. These effects on m_i s may be attributed principally to the polarities of materials. The mass ratio of the solvent relative to the feed, E_0/R_0 did not affect the m_i s.

The mass fractions of water in R_0 and R measured about 10^{-4} and 10^{-3} in the cases of AO and TLO, respectively. The leakage of water from the solvent to the raffinate phase was, therefore, favorably low.

2.5 Simultaneous separation process

Figure 3 schematically demonstrates the simultaneous separation process with a single solvent. The original AO contacts with the solvent of aqueous methanol solution loaded with the extractives from TLO, mainly pyridine. In this contact, quinolines and indole in AO are extracted into the aqueous solvent phase and the pyridine in the aqueous phase, into AO phase. The raffinate AO consists mainly of pyridine, bicyclic aromatic hydrocarbons, and dibenzofuran. Since the boiling point of these components are different from one another as listed in Table 2, the raffinate AO can be distilled ordinarily into several groups of components. In the other contact, the aqueous phase from the contact with AO releases the extractives from AO into TLO and extracts pyridine from TLO. The raffinate TLO composed of quinolines, indole, and monocyclic aromatics can also be separated by ordinary distillation. Consequently, the separations both of AO and TLO can be attained simultaneously with a single solvent.

Conclusion

The distribution coefficients of the components contained in absorption oil and tar light oil were roughly classified by magnitude into four groups of components, that is, these decreased in the order of pyridine, quinolines and indole, monocyclic aromatics, and bicyclic aromatics and dibenzofuran. The coefficient in the case of absorption oil as an oil phase was almost equivalent to that in the case of tar light oil. These results and the physical properties of the components led to the process of simultaneous separations of absorption oil and tar light oil with a single solvent.

Acknowledgement

JFE Chemical Corporation supplied absorption oil and tar light oil.

Nomenclature

E =mass of aqueous phase[kg] ; m =distribution coefficient [-] ;

R =mass of oil phase [kg] ; x =mass fraction in oil phase [-] ; y =mass fraction in aqueous phase [-]

<Subscripts>

0=at initial ; 1MN=1-methylnaphthalene ; 2MN=2-methylnaphthalene ; B= benzene ; BP=biphenyl ; DBF=dibenzofuran ; EB=ethylbenzene ; I=indole ; In=indene ; IQ=isoquinoline ; i=component i ; MeOH=methanol ; N=naphthalene ; Pr=pyridine ; Q=quinoline ; T=toluene ; W=water ; X=xylene

Literature Cited

- 1) Ukegawa, K., *et al.*, *J. of JPI*, **33**, (4), 250 (1990)
- 2) Kodera, Y., *et al.*, *Fuel*, **70**, (6), 765 (1991)
- 3) Matsumura, A., *J. of NIRE*, **4**, (2), 43 (1995)
- 4) Egashira, R. and M. Nagai, *J. of JPI*, **43**, (5), 339 (2000)
- 5) Egashira, R. and C. Salim, *J. of JPI*, **44**, (3), 178 (2001)
- 6) Egashira, R., M. Nagai, and C. Salim, 6th World Congress of Chemical Engineering, 1306 (2001, Melbourne)
- 7) Salim C., Master Thesis, Tokyo Institute of Technology (2002)

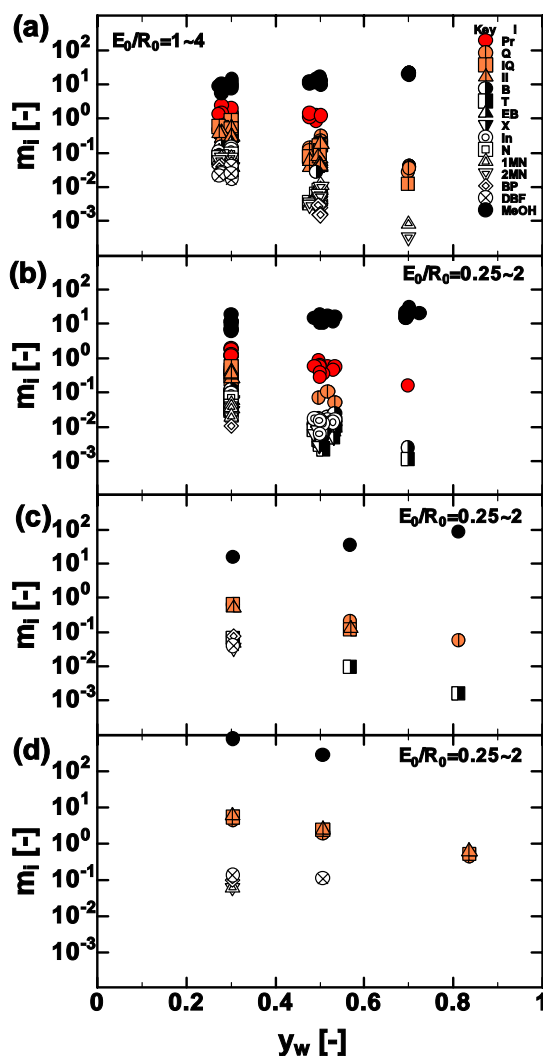


Fig.2 Effect of water content in aqueous phase, y_w , on distribution coefficient, m_i , in the cases of (a) absorption oil; (b) tar light oil; (c) toluene⁷⁾; and (d) heptane⁷⁾



Fig.3 Simultaneous separation process with a single solvent