SEPARATION OF COAL TAR ABSORPTION OIL BY O/W/O LIQUID MEMBRANE

SHIMADA YOSHIYUKI
Student ID : 03-1226-0
Supervisor: EGASHIRA RYUICHI
Department of International Development Engineering, School of Engineering,
Tokyo Institute of Technology, Tokyo 152-8552, Japan

Introduction

Coal tar includes more than 400 compounds. Coal tar absorption oil (AO), which is one of the fractions obtained by distillation of the coal tar, is mainly composed of nitrogen heterocyclic compounds such as quinoline (Q), isoquinoline, indole etc, homocyclic compounds such as 1-methylnaphtalene, 2-methyl-naphtalene (2MN), biphenyl etc, and a small quantity of oxygen heterocyclic compounds such as dibenzo-furan etc. These compounds are utilized as raw materials for agricultural chemicals, medicines, perfumes, and many other useful chemicals. The separation of these compounds is carried out in the following two steps: the first step is rough separation of AO by acidic and basic extraction method: the second is further separation into respective components and purification by other method, such as crystallization. However, this acidic and basic extraction used in the first step has some drawbacks: corrosion of the equipments, difficulty in solvent recovery, and so on. To solve these problems in AO rough separation, several alternative methods such as liquid-liquid extraction, liquid membrane etc, have been studied.

In this work, batch runs of permeation through O/W/O emulsion liquid membrane were carried out in a stirred vessel with the feed of ternary model mixture to study the effects of material systems of feed, membrane liquid, and solvent on permeation.

1. Experimental

a) Emulsification
The experimental apparatus for emulsification is illustrated in **Figure 1(a)**. The experimental conditions are summarized in **Table 1**. Ternary model mixtures (feed1: Q-2MN-Hp, feed2: Q-2MN-T) were used as feed oils. Aqueous solution of saponin, emulsifying agent, and 1,3-butanediol, enhancing the dissolutions of permeates was used as a membrane liquid. The feed oil and membrane liquid were stirred with commercial high-speed homogenizer (SMT Multi Disperser, SMT Corp.) to prepare the emulsion.
b) Permeation
The experimental apparatus for permeation is illustrated in **Figure 1(b)**. The permeator was a vessel made of Pyrex glass equipped with an impeller and with four baffles. The prepared feed emulsion and the solvent (Heptane for using feed1, Toluene for using feed2) were poured into the permeator, and then stirring was started (t=0). The solvent phase was sampled at specified operation time and was analyzed by a gas chromatograph to determine the composition.

2. Results and Discussion

Figure 2 shows the time courses of y_Q and y_{2MN} with feed1. In all cases, y_Q were higher than y_{2MN}, despite that $x_{Q,0}$ were about one third of $x_{2MN,0}$, and quinoline and 2-methylnaphthalene could be separated into each other. Figure 2 shows the effect of 1,3-butanediol in the membrane on the permeation. y_Q and y_{2MN}, that is, permeation rates in the case with 1,3-butanediol were higher than those without 1,3-butanediol, since the

Table 1 Experimental conditions for batch separation with emulsion liquid membrane

Feed	Quinoline-2Methylnaphthalene-Heptane (feed1), x_Q=0.08, x_{2MN}=0.25		
	Quinoline-2Methylnaphthalene-Toluene (feed2), x_Q=0.08, x_{2MN}=0.25		
Membrane	Aqueous solution of Saponin and 1,3-butanediol		
Additives	Saponin (CS=0.005, 0.025, 0.03), 1,3-butanediol (C_{13B}=0, 0.25)		
Solvent	Heptane (for feed1), Toluene (for feed2)		
Stirring velocity in emulsification	N_1	[h⁻¹]	1.1×10^5
Stirring velocity in permeation	N_p	[h⁻¹]	1.8×10^4
Total volume of liquid in permeator	V_T	[m³]	4.0×10^{-4}
Volume fraction of inner oil phase in O/W emulsion	α_{WO}	[-]	0.5
Volume fraction of O/W emulsion	α_O	[-]	0.25
Operation time	t	[h]	0–0.044
Operation temperature	T	[K]	298±5

(a)   (b)
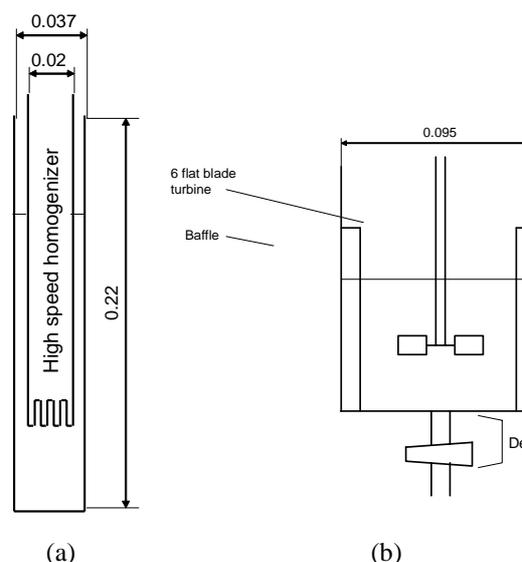
Fig.1 Schematic diagram of experimental apparatus: (a) for arrangement of emulsion; (b) batch emulsion liquid permeation
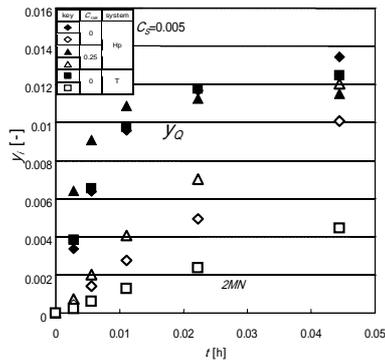
Fig.2 Time courses of y_Q and y_{2MN}
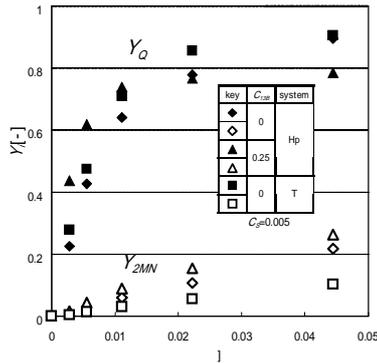
Fig.3 Time courses of yields, Y_i
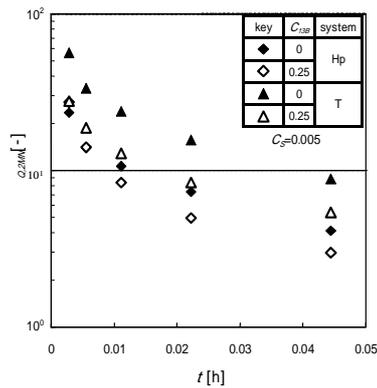
Fig.4 Time courses of separation selectivity of quinoline relative to 2-methylnaphthalene $\beta_{Q,2MN}$

distribution coefficients of permeates increased with 1,3-butanediol[3]. The effect of material system of feed and solvent is also shown in Fig.2, since the distribution coefficients of permeates increased with 1,3-butanediol[3). Permeation rate of quinoline in the case of feed1 was slightly higher than that of feed2 and permeation rate of 2-methylnaphthalene in the case of feed1 was higher than that of feed2, since the distribution coefficients of permeates increased in the case of feed1[2). The yield of component i, Yi, and the separation selectivity of quinoline relative to 2-methyl-naphthalene, $\beta_{Q,2MN}$, were defined as,

$$Y_i = \frac{E \cdot y_i}{R_0 \cdot x_{i,0}} \tag{1}$$

$$\beta_{Q,2MN} = \frac{Y_Q}{Y_{2MN}} \tag{2}$$

with the mass and mass fractions of feed and extract.

Figure 3 shows time courses of the yields of component i, Y_i, calculated by Eq.(1). Y_Q was much higher than Y_{2MN} and it was confirmed again that these two components could be separated by this technique. The yields in the case with 1,3-butanediol were higher than those without 1,3-butanediol. The effect of material system of feed and solvent is also shown in Fig.3. Y_Q in the case of feed1 was higher than that of feed2 and Y_{2MN} in the case of feed1 was lower than that of feed2. Y_Q reached around 0.9 at highest in the case of feed2. **Figure 4** shows the time courses of the separation selectivities of quinoline relative to 2-methylnaphtha-lene. $\beta_{Q,2MN}$ decreased with 1,3-butanediol in the membrane or in the case of feed1. In the case of feed 2 without 1,3-butanediol, the highest $\beta_{Q,2MN}$ was 56.

Conclusion

Permeation rates and yields increased in the case with 1,3-butandiol in the membrane. Permeation rate and yield of quinoline increased in the case of feed2. Those of 2-methylnaphthalene decreased in the case of material system of feed2. The separation selectivities of quinoline relative to 2-methylnaphthalene decreased in the case with 1,3-butandiol in the membrane or in the case of feed1.

Nomenclature

C_S	=mass fraction of saponin in aqueous membrane phase	[-]
C_{13B}	=mass fraction of 1,3-butanedol in aqueous membrane phase	[-]
E	=mass of extract	[kg]
R	=mass of raffinate	[kg]
x	=mass fraction in raffinete phase	[-]
Yi	=yield of component i	[-]
y	=mass fraction in extract phase	[-]
$\beta_{Q,2MN}$	= separation selectivity of Q relative to 2MN	[-]

<Subscript>
0 =initial
2MN=2-methylnaphtalene
i =component i
Q   =quinoline

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