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Nomenclature

a	= volume fraction of fluid 1 ($=C_a/C_{a0}$)	[—]
b	= volume fraction of fluid 2 ($=C_b/C_{b0}$)	[—]
C	= concentration	[mol/l]
D_m	= mass diffusivity	[cm ² /sec]
d	= diameter of impeller	[cm]
g	= simultaneous frequency function of age and life expectation	[—]
I_s	= intensity of segregation	[—]
J	= degree of segregation based on age	[—]
k_r	= reaction rate constant	[l/(mol·sec)]
N_p	= power number	[—]
n	= impeller speed	[r.p.s.]
p	= micromixing parameter	[—]
Q	= volumetric flow rate	[cm ³ /sec]
q	= micromixing parameter	[—]
Re	= Reynolds number	[—]
Sc	= Schmidt number	[—]
s	= segregation function	[—]
V	= volume of tank reactor	[cm ³]
α	= age	[sec]
ε	= turbulent kinetic energy dissipation rate per unit mass	[cm ² /sec]

λ	= life expectation	[sec]
λ_s	= microscale of turbulence	[cm]
ν	= kinematic viscosity	[cm ² /sec]
ρ	= density of reactant solution	[g/cm ³]
τ	= mean residence time	[sec]
ϕ_L	= life expectation distribution	[—]

<Subscripts>

a	= reactant A
b	= reactant B
E	= entering environment
e	= exit
L	= leaving environment
0	= time zero or initial time
1	= fluid 1
2	= fluid 2

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COMBINED PROCESS OF REACTION, EXTRACTION AND DISTILLATION

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Introduction

In conventional chemical plants, processes to which different functions, such as reaction, extraction, distillation are assigned used to be treated independently of others except in some limited cases, e.g. the combination of reaction and heat exchange. But, under certain conditions, many other combined processes in which two or more operations are simultaneously processed might be preferable to the successive combination of conventional unit operations. For ex-

ample, in esterification, a reactive distillation^{1,2)} and an extractive reaction³⁾ were investigated to obtain conversions higher than that for chemical equilibrium. For separation of mixtures having a very low relative volatility, an extractive distillation is often employed to change the relative volatility by adding another solvent.

In this paper, some basic considerations are given for assuring the advantage of the combined process where the three operations of reaction, extraction and distillation are simultaneously carried out. This combined operation which is referred to as reactive extractive distillation, is compared with three other processes, that is, reactive distillation, extractive

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reaction and reaction without simultaneous separation, in view of the yield of desired intermediate of the complex reaction in a stirred vessel.

Problem Formulation

Let us consider a single stirred tank involving two liquid phases and one vapor phase, as shown in Fig. 1. Two insoluble solvents form a reactive phase in which the reaction proceeds, and an extractive phase in which the extraction of desired product takes place. One of the two liquid phases is a dispersed phase and the other a continuous phase. The concentrations in each phase are homogeneous and the system is isothermal. The reactive and extractive phases are heated in their respective feed lines and their vapors evolve. For the reactive phase, the ratio of the vapor evolution rate, v_1 , to the liquid feed flow rate, g_{1f} , is equal to $(1-q_1)$. Similarly, for the extractive phase, the ratio of v_2 to g_{2f} is equal to $(1-q_2)$.

The reaction considered is a combination of reversible and consecutive reactions which are of the first order, that is,

where R is the desired product and S the by-product.

The reaction rates in the reactive phase are

$$r_{A1} = -kC_{A1} + k'C_{R1} = -kC_{t1}x_{A1} + k'C_{t1}x_{R1} \quad (1)$$

$$r_{R1} = kC_{A1} - (k' + k'')C_{R1} = kC_{t1}x_{A1} - (k' + k'')C_{t1}x_{R1} \quad (2)$$

It is assumed that no reactions occur in the vapor and extractive phases.

Mass balances of A and R around the stirred tank are

$$g_{1f}x_{A1,f} + g_{2f}x_{A2,f} = g_1x_{A1} + g_2x_{A2} + v y_A - r_{A1}V_1 \quad (3)$$

$$0 = g_1x_{R1} + g_2x_{R2} + v y_R - r_{R1}V_1 \quad (4)$$

where the concentrations of R at feed are zero.

Since the rate of mass transfer between each liquid and vapor phase is usually much higher than that of chemical reaction, vapor-liquid equilibrium is assumed and the equilibrium relationship is expressed in terms of the activity coefficient, γ . For the reactant, A, we have

$$P_t y_A = \gamma_{A1} P_A x_{A1} \\ = \gamma_{A2} P_A x_{A2}$$

where P_t is the total pressure and P_A the vapor pressure of A. Rewriting these equations yields

$$x_{A2} = (\gamma_{A1}/\gamma_{A2})x_{A1} = K_A x_{A1} \quad (5)$$

$$y_A = (\gamma_{A1} P_A / P_t) x_{A1} = K_A^* x_{A1} \quad (6)$$

Similarly, for the intermediate, R, we have

$$x_{R2} = (\gamma_{R1}/\gamma_{R2})x_{R1} = K_R x_{R1} \quad (7)$$

$$y_R = (\gamma_{R1} P_R / P_t) x_{R1} = K_R^* x_{R1} \quad (8)$$

Fig. 1 Schematic of reactive-extractive distillation

For simplicity, activity coefficients are assumed to be independent of the concentrations and therefore K_A , K_A^* , K_R and K_R^* are constant. Since the mass transfer between two liquid phases is usually slower than that between vapor and liquid phases, it seems reasonable that the relationships of concentrations between two liquid phases are given by Eqs. (5) and (7) which depend only on the vapor-liquid equilibrium relationships. Therefore, the constants, K_A and K_R are generally different from the distribution coefficients of liquid-liquid equilibrium, m_A and m_R .

By substituting Eqs. (1), (2), (5)–(8) into Eqs. (3) and (4) and by reducing to dimensionless equations, we have

$$\zeta x_{A1,f} + (1-\zeta)x_{A2,f} = (\beta_A + \tau)x_{A1} - \kappa_R \tau x_{R1} \quad (9)$$

$$0 = -\tau x_{A1} + \{\beta_R + (\kappa_R + \kappa_C)\tau\}x_{R1} \quad (10)$$

where

$$\beta_A = (g_1 + g_2 K_A + v K_A^*) / (g_{1f} + g_{2f}) \\ = q_1 \zeta + q_2 (1-\zeta) K_A + \{(1-q_1)\zeta + (1-q_2)(1-\zeta)\} K_A^* \quad (11)$$

$$\beta_R = (g_1 + g_2 K_R + v K_R^*) / (g_{1f} + g_{2f}) \\ = q_1 \zeta + q_2 (1-\zeta) K_R + \{(1-q_1)\zeta + (1-q_2)(1-\zeta)\} K_R^* \quad (12)$$

$$\zeta = g_{1f} / (g_{1f} + g_{2f}) \quad (13)$$

$$\tau = k C_{t1} V_1 / (g_{1f} + g_{2f}) \quad (14)$$

$$\kappa_R = k' / k \quad (15)$$

$$\kappa_C = k'' / k \quad (16)$$

Optimization

The yield of the intermediate, R, is defined as the ratio of the resultant production rates of R from vapor and liquid phases to the feed flow rates of A;

$$\eta = (g_1 x_{R1} + g_2 x_{R2} + v y_R) / (g_{1f} x_{A1,f} + g_{2f} x_{A2,f})$$

By using Eqs. (7), (8) and (12), we have

$$\eta = (g_1 + g_2 K_R + v K_R^*) x_{R1} / (g_{1f} x_{A1,f} + g_{2f} x_{A2,f}) \\ = \beta_R x_{R1} / \{\zeta x_{A1,f} + (1-\zeta)x_{A2,f}\}$$

Further, by substituting x_{R1} derived from Eqs. (9) and (10), we obtain

$$\eta = \beta_R \tau / [\kappa_C \tau^2 + \{\beta_A (\kappa_R + \kappa_C) + \beta_R\} \tau + \beta_A \beta_R] \quad (17)$$

Referring to Eqs. (11) and (12), we have four decision variables, τ , ζ , q_1 and q_2 , and six parameters, K_A , K_R , K_A^* , K_R^* , κ_R and κ_C in Eq. (17). The value of

Facet DEFG ($\zeta = 1$) : Reactive distillation
 Edge BF ($q_1 = q_2 = 1$) : Extractive reaction
 Edge EF ($\zeta = q_1 = 1$) : Reaction

Fig. 2 The feasible region of ζ , q_1 and q_2 for the reactive extractive distillation

each parameter is fixed if the reaction system, temperature and pressure are specified, whereas the value of each decision variable is adjustable by changing the operating conditions.

The value of τ which maximizes the value of η can easily be determined as

$$\tau = \sqrt{\beta_A \beta_R / \kappa_C} \quad (18)$$

Substitution of Eq. (18) into Eq. (17) yields

$$\eta = 1 / \{ (\kappa_R + \kappa_C) \phi + 1 + 2 \sqrt{\kappa_C} \sqrt{\phi} \} \quad (19)$$

where

$$\begin{aligned} \phi &= \beta_A / \beta_R \\ &= \frac{q_1 \zeta + q_2 (1 - \zeta) K_A + \{ (1 - q_1) \zeta + (1 - q_2) (1 - \zeta) \} K_A^*}{q_1 \zeta + q_2 (1 - \zeta) K_R + \{ (1 - q_1) \zeta + (1 - q_2) (1 - \zeta) \} K_R^*} \end{aligned} \quad (20)$$

In the case of extractive reaction for which $q_1 = q_2 = 1$, K_A and K_R in Eq. (20) must be replaced by m_A and m_R , respectively, as is pointed out previously. Therefore, Eq. (20) reduces to

$$\phi = \{ \zeta + (1 - \zeta) m_A \} / \{ \zeta + (1 - \zeta) m_R \} \quad (21)$$

Eq. (19) indicates that the maximization of η reduces to the minimization of ϕ with respect to the remaining three variables, ζ , q_1 and q_2 . Since all these variables can be varied from zero to unity, the feasible region is the unit cube such as shown in Fig. 2. If we direct our attention to only one of these variables, we see that Eq. (20) or Eq. (21) has the form of

$$\phi = (a\chi + b) / (c\chi + d) \quad (22)$$

with respect to any one of them. It is clear that the ϕ in Eq. (20) or Eq. (21) is monotone increasing, monotone decreasing and constant according to $(ad - bc)$ being positive, negative and equal to zero, respectively. Therefore, the minimal value of ϕ must generally occur on the boundary of the cubic feasible region although under some special circumstances such as $K_A/K_R = K_A^*/K_R^* = 1$ and $m_A/m_R \leq 1$ the same

minimal value of ϕ is taken in the interior as well as on the boundary of the feasible region.

Now, consider the value of ϕ on the facet OABC in Fig. 2. Since $\zeta = 0$ on this facet, Eqs. (20) and (21) reduce to

$$\phi = \{ q_2 K_A + (1 - q_2) K_A^* \} / \{ q_2 K_R + (1 - q_2) K_R^* \} \quad (23)$$

and

$$\phi = m_A / m_R \quad (24)$$

respectively. The ϕ in Eq. (23) is independent of q_1 and the minimal value of ϕ will generally occur either on the edge OA or the edge BC because ϕ is monotonous with respect to q_2 .

The ϕ takes the minimal value

$$\phi = K_A^* / K_R^* \text{ on the edge OA } (q_2 = 0)$$

if $K_A/K_R > K_A^*/K_R^*$ and the minimal value

$$\phi = K_A / K_R \text{ on the edge BC } (q_2 = 1)$$

if $K_A/K_R < K_A^*/K_R^*$.

In the special case of $K_A^*/K_R^* = K_A/K_R$, the ϕ is constant at every point on the facet OABC. In the discussion above, it is assumed that m_A/m_R is larger than both K_A/K_R and K_A^*/K_R^* . If this is not the case, the minimal value of ϕ on the facet OABC occurs at the vertex B.

After the similar investigations about the remaining facets of the feasible cube, the candidates for the minimal value of ϕ are obtained as shown in Fig. 2.

Conclusions

It is evident from Fig. 2 that the minimal value of ϕ is the smallest of four values, 1, m_A/m_R , K_A^*/K_R^* and K_A/K_R which can occur on the edge EF, at the vertex B, on the edges OA, OD and DG and on the edge BC, respectively. Therefore, the following conclusions are deduced:

(i) Since the edge EF corresponds to the reaction without simultaneous separation, any combined process is useless if the value 1 is the smallest.

(ii) Since the edge BF corresponds to the extractive reaction, the optimal combined process is the extractive reaction if the value m_A/m_R is the smallest.

(iii) Since the facet DEFG corresponds to the reactive distillation, the optimal combined process is reactive distillation if the value K_A^*/K_R^* is the smallest.

(iv) Reactive extractive distillation which includes all three phases in the stirred tank can be optimal on the edge BC (except the vertex B) only if the value K_A/K_R is the smallest.

Since $\zeta = 0$ and $q_2 = 1$ on the edge BC, there are no flow of reactive and vapor phases, and only the extractive liquid phase is flowing. But it is necessary to maintain three phases in the stirred tank because the reaction can take place only in the reactive phase, and in addition, the values of K_A and K_R come from

vapor-liquid equilibrium. This requirement will be satisfied by the recirculation of reactive phase from a separator of the discharged liquid phases, and by using the closed stirred tank for maintaining the vapor phase. It will, however, be necessary in practice to feed make-up of reactive and vapor phases to the tank.

To improve the yield of the desired product, it is important to choose the two solvents having the value of K_A/K_R , K_A^*/K_R^* or m_A/m_R which is as small as possible.

Nomenclature

C	= concentration	[g-mole/cm ³]
g	= liquid flow rate	[g-mole/sec]
K_A	= γ_{A1}/γ_{A2}	[—]
K_R	= γ_{R1}/γ_{R2}	[—]
K_A^*	= $\gamma_{A1}P_A/P_t$	[—]
K_R^*	= $\gamma_{R1}P_R/P_t$	[—]
k, k', k''	= rate constant of first order reaction	[1/sec]
m	= distribution coefficient	[—]
P	= pressure	[atm]
$1-q$	= ratio of evolution rate of vapor to the liquid flow rate at feed	[—]
r	= reaction rate	[g-mole/sec·cm ³]
V	= volume	[cm ³]
v	= vapor flow rate	[g-mole/sec]

x	= mole fraction in liquid phase	[—]
y	= mole fraction in vapor phase	[—]
β_A	= defined by Eq. (11)	[—]
β_R	= defined by Eq. (12)	[—]
γ	= activity coefficient	[—]
ζ	= $g_{1f}/(g_{1f}+g_{2f})$	[—]
η	= yield defined by Eq. (17)	[—]
κ_R	= k'/k	[—]
κ_O	= k''/k	[—]
τ	= defined by Eq. (14)	[—]
ϕ	= modulus defined by Eqs. (20) and (21)	[—]

<Subscripts>

A	= reactant, A
f	= feed
R	= product, R
t	= total
1	= reactive phase
2	= extractive phase

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ABSTRACTS OF KAGAKU KOGAKU RONBUNSHU VOL. 2, NO. 4, JULY, 1976

Light Scattering Aerosol Measurements for Absorbing Particles, Akira Kanagawa (Nagoya Univ.)

Kagaku Kogaku Ronbunshu, **2**, 325–330 (1976)

A discussion based on exact Mie theory calculations is given on light scattering aerosol measurements for absorbing aerosol particles. From the calculations of Mie's scattering light intensity functions for absorbing particles as a variable of imaginary part of refractive index, it has been found that the scattering light intensities vary abruptly with the variance of imaginary parts in the region from 0 to 0.2 of their value. Response calculations for the aerosol particle photometer for particle sizing and the aerosol photometer for particle concentration measurement have been made for absorbing particles. As a result, it is pointed out that one should take into account the absorbing properties of aerosol particles on the light scattering aerosol measurement, particularly when the particle size is greater than 1 μm .

Size Determination of Submicron Particles by Owl-Type Photometer, Akira Kanagawa and Takeshi Takahashi (Nagoya Univ.)

Kagaku Kogaku Ronbunshu, **2**, 331–335 (1976)

A Owl-type photometer designed for measuring the particle

size of monodispersed submicron particles was constructed and has been used experimentally for polystyrene latex hydrosols. The angular dependency of the ratio R_1 of the long-wavelength scattering light intensity vertically polarized to the short one are measured and compared with the theoretical relations calculated from Mie's scattering theory.

As a result, it was found that the pattern of the angular dependency of R_1 varies regularly with particle size, and this photometer seems to be capable of the size determination roughly of monodispersed particles in hydrosols.

Quite similar studies of the angular dependency of the polarization ratio of the scattering light were made also, and similar results were obtained.

Anisokinetic Sampling Errors for Aerosols, Hideto Yoshida, Hiroaki Masuda, Koichi Iinoya (Kyoto Univ.), Takeshi Ohsugi (Nihon Kogyo Co., Ltd.) and Shinichi Yuu (Kyushu Inst. of Tech.)

Kagaku Kogaku Ronbunshu, **2**, 336–340 (1976)

To examine the error in measuring particle concentration due to anisokinetic sampling over a wide range of inertial parameters,