DESIGN OF APPARATUS FOR SEPARATING HOMOGENEOUS LIQUID MIXTURES ON POLYMER FILMS

V. G. Gorskii, R. G. Kocharov, and V. Z. Brodskii

Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 3, pp. 314–320, 1967

UDC 66.05

The proposed design method makes it possible to determine the necessary film area and estimate the suitability of a particular separation process on the basis of data that can readily be obtained experimentally.

In recent years, the separation of liquid mixtures on polymer films has become increasingly popular. Such processes as the desalination of sea water, the separation of saturated and unsaturated hydrocarbons, the separation of gasoline fractions, the removal of water from organic alcohols, ketones, and aldehydes, etc., have begun to develop rapidly [1].

The separation of azeotropic mixtures and mixtures whose components have similar boiling points is of special interest [2–7]. It has been shown [2–5] that, in a series of cases, separation on polymer films can successfully compete with azeotropic and extractive distillation. Foreign scientists have already built semi-industrial installations with a film area of several tens of square meters for separating such azeotropic mixtures as isopropanol-water, pyridine-water, and isopropanol-ethanol-water.

In the Soviet Union, a new method of separation is also about to be introduced industrially. Thus, joint research in the Department of Processes and Apparatus of the Moscow Mendeleev Chemical Engineering Institute and the Laboratory of Processes and Apparatus of the All-Union Glass-Fiber Scientific-Research Institute has shown that polymer films can be used to separate caprolactam from the wash water of polyamide fiber plants. The test results have been used as a basis for developing variants of the apparatus and designing a pilot plant on which caprolactam regeneration experiments have been carried out [9].

We are investigating the use of polymer films for removing water from a number of organic liquids and for other purposes.

However, the application of this separation method encounters a number of difficulties. In particular, most publications are devoted exclusively to a study of the permeability mechanism and give no indication concerning the choice of the optimum form of apparatus or the calculation of the necessary film area. Thus, the effect of the hydrodynamic conditions on the process is discussed only in [8, 9, 11]. The few attempts to develop a method of calculating the necessary film area [2, 10] have been only partially effective and do not make it possible to compare different techniques.

In this paper, we propose a method of calculating batch-type and continuous-flow apparatus for separating homogeneous liquid mixtures by means of polymer films.

Theoretical. The process of separation of homogeneous binary liquid mixtures using polymer films is based on the different rates of diffusion of the components through the film and consists of three stages 1) absorption of the mixture components into the film from the liquid phase; 2) diffusion of the molecules through the polymer structure; 3) evaporation of the molecules from the opposite side of the film.

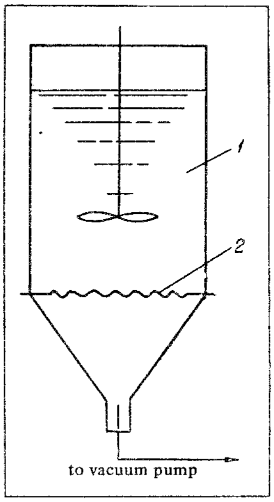

Fig. 1. Batch-type apparatus with liquid-phase mixing: 1) separating chamber; 2) polymer film.

The separation process can be carried out in apparatus of various types—both intermittent and continuous. We will consider some special cases.

Batch apparatus with liquid-phase mixing. This apparatus is shown schematically in Fig. 1. The mixture to be separated is poured into the working chamber 1, where it is vigorously mixed, so that the composition of the mixture is constant at all points of the chamber. Vapor which penetrates film 2 is drawn off by a vacuum pump.

When this process takes place under constant specific conditions, it can be described by means of the following system of equations:

$$G + L = L_0, \tag{1}$$

$$Gx^G + Lx^L = L_0x_0^L, \tag{2}$$

$$\frac{d(Gx^G)}{dG} = \xi, \tag{3}$$

$$\xi = g(x^L), \tag{4}$$

$$\frac{dG}{F d\tau} = f(x^L). \tag{5}$$

Here, (1) and (2) are the material balance equations for the mixture as a whole and the more readily diffusing component, respectively; Eq. (3) gives the relation between the instantaneous selectivity ξ and the quantity x^G; Eqs. (4) and (5) give the instantaneous selectivity and throughput as functions of the concentration of the liquid in the apparatus.

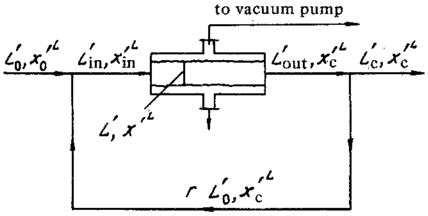

Fig. 2. Diagram of a continuous-flow apparatus.

Hence, we find that

$$\frac{L}{L_0} = \exp \lambda(x^L), \tag{6}$$

$$\frac{G}{L_0} = 1 - \exp \lambda(x^L), \tag{7}$$

$$\frac{F\tau}{L_0} = \int_{x_0^L}^{x^L} \frac{\exp \lambda(x^L)}{f(x^L)[x^L - g(x^L)]} dx^L, \tag{8}$$

where

$$\lambda(x^L) = \int_{x_0^L}^{x^L} \frac{dx^L}{g(x^L) - x^L}.$$

Assigning x^L, we can use the first two equations to calculate L/L_0 and G/L_0. Using (8), we can calculate the film area necessary to separate a certain amount of mixture in a given time. The functions $g(x^L)$ and $f(x^L)]$ required for the calculation can easily be obtained experimentally.

Continuous-flow apparatus. This apparatus is shown schematically in Fig. 2 for the most general case. The solution to be separated passes through a chamber bounded on two sides by polymer films. Part of the output solution, enriched in the less readily diffusing component, is recycled. The relative amount of recirculating solution is given by the recycle ratio r.

We make the following assumptions: 1) the motion of the liquid in the chamber is such as to exclude mixing in the direction of flow while ensuring perfect mixing in the transverse direction; 2) the process takes place under specific stationary conditions. In this case, the process can be described by the following system of equations:

$$G' + L' = L'_{in}, \tag{9}$$

$$G'x'^G + L'x'^L = L'_{in} x'^L_{in}, \tag{10}$$

$$\frac{d(G'x'^G)}{dG'} = \xi, \tag{11}$$

$$\xi = g(x'^L), \tag{12}$$

$$\frac{dG'}{dF} = f(x'^L), \tag{13}$$

$$L'_{in} = (1 + r) L'_0, \tag{14}$$

$$x'^L_{in} = x'^L_c - \frac{x'^L_c - x'^L_0}{1 + r}, \tag{15}$$

$$L'_{out} = L'_c + rL'_0. \tag{16}$$

From this system, after simple transformations, we find equations analogous to (6) and (7):

$$\frac{L'}{L'_0} = (1 + r) \exp\left[\lambda(x'^L) - \lambda(x'^L_{in})\right],$$

$$\frac{G'}{L'_0} = (1 + r)\left\{1 - \exp[\lambda(x'^L) - \lambda(x'^L_{in})]\right\},$$

where $\lambda(x'^L) = \int_{x_0'^L}^{x'^L} \frac{dx'^L}{g(x'^L) - x'^L}$, and we also have

$$\frac{F}{L'_0} = (1 + r) \exp\left[-\lambda(x'^L_{in})\right] \times$$

$$\times \int_{x'^L_{in}}^{x'^L_c} \frac{\exp \lambda(x'^L)}{f(x'^L)[x'^L - g(x'^L)]} dx'^L. \tag{17}$$

Using this equation, we can obtain the film area required for separation at any recycle ratio.

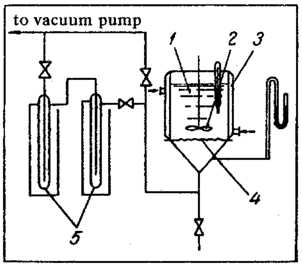

Fig. 3. Diagram of a laboratory apparatus for separating liquid mixtures by means of polymer films: 1) separating chamber; 2) paddle mixer; 3) heating jacket; 4) polymer film; 5) traps.

When r → 0, we obtain

$$\frac{F}{L'_0} = \exp[-\lambda(x'^L_0)] \int_{x'^L_0}^{x'^L_c} \frac{\exp \lambda(x'^L)}{f(x'^L)[x'^L - g(x'^L)]} dx'^L. \tag{18}$$

Transforming (17) for the case in which r → ∞, we arrive at the equation

$$\frac{F}{L'_0} = \frac{x'^L_c - x'^L_0}{f(x'^L_c)[x'^L_c - g(x'^L_c)]}. \tag{19}$$

Equation (17) and the derived equation (18) were obtained on the assumption that there is no mixing in the direction of flow but perfect mixing in the transverse direction. A more accurate solution can be obtained by taking into account both transverse and longitudinal diffusion in the flow.

Experimental. To compare the theoretical calculations with experimental observations, we conducted experiments on the separation of a glycerol-water mixture on cellophane in a batch-type apparatus with mixing of the liquid phase. This mixture was selected on account of the low volatility of the components and the simplicity of analysis (on a refractometer), which reduced the experimental errors. The apparatus is shown schematically in Fig. 3. The starting solution was poured into separation chamber 1, where it was vigorously mixed by paddle mixer 2. The temperature was regulated correct to ±0.2° C by passing hot water through jacket 3. Vapor passing through film 4 was drawn off by a vacuum pump and condensed in traps 5, where a temperature of −70° C was maintained. The pressure on the vapor phase side was kept in the range 3200–3400 N/m^2, and on the liquid phase side, at atmospheric pressure. The thickness of the film in the unswollen state was $45\,\mu$, and the working area was 0.0023 m^2.

We first recorded the functions $g(x^L)$ and $f(x^L)$. For this purpose, we introduced solutions of different concentrations into the separating chamber in relatively large amounts. The duration of the experiments was kept short enough for the concentration of the starting solution to remain essentially unchanged. In this case, we measured the amount of liquid passing through the film and its composition, which was taken as the instantaneous selectivity for the time-average concentration of starting solution during the experiment. The data obtained at a liquid temperature of 50° C are presented in the table.

We then performed an experiment representing the batch process proper. An aqueous glycerol solution in the amount of 0.2 kg at a concentration $x_0^L = 0.90$ was introduced into the separating chamber. The separation experiment was continued for 6 hr. The temperature and pressure were kept the same as in recording the functions $g(x^L)$ and $f(x^L)$. The concentration of the liquid at the end of the experiment was $x_c^L = 0.71$. We then made a theoretical calculation of the time required to separate 0.2 kg of mixture from $x_0^L = 0.90$ to $x_c^L = 0.71$ in an apparatus with a film area $F = 0.0023$ m^2 using the relations $f(x^L)$ and $g(x^L)$. The calculation was made graphically and analytically. We obtained $\tau = 6.0$ hr.

Thus, the calculated value of the time required for separation and the experimental value coincided.

To estimate the efficiency of apparatus of different types, it is necessary to calculate the film area required for separation on the basis of $f(x^L)$ and $g(x^L)$ using Eqs. (8), (18), and (19). Employing these equations, we worked out a numerical example (see [2]) on the separation of an isopropanol-water mixture. It was found that, in this case, carrying out the process in an apparatus represented by Eq. (18) requires a film area smaller by a factor of approximately 1.5 in comparison with that for a perfect-mixing apparatus (Eq. (19)).

Values of the Function $f(x^L)$ at Different Concentrations of the Starting Solution, $g(x^L) = 1$

x^L	$f(x^L) \cdot 3.6 \cdot 10^3$
1.00	13.5
0.90	11.1
0.85	9.9
0.80	8.8
0.75	7.7
0.71	6.9
0.70	6.7

NOTATION

G is the amount of mixture passing through film in time τ, kg; x^G is the weight fraction of more readily diffusing component (component A) in the total amount of mixture passing through the film in time τ; L is the amount of mixture remaining in the apparatus after time τ, kg; x^L is the weight fraction of component in this mixture; L_0 is the starting amount of mixture introduced into the apparatus, kg; x_0^L is the weight fraction of component A in this mixture; ξ is the weight fraction of component A in the mixture passing through the film in the time interval from τ to $\tau + d\tau$ (instantaneous selectivity); F is the film area, m^2; L_0' is the amount of the mixture supplied to the system per unit time, kg/sec; $x_0'^L$ is the weight fraction of component A in this mixture; L'_{in} is the amount of the mixture supplied to the separating chamber per unit time, kg/sec; $x_{in}'^L$ is the weight fraction of component A in this mixture; L' is the amount of the mixture passing per unit time through a cross section at distance l from the chamber inlet, kg/sec; x'^L is the weight fraction of component A in the flow in this section; L'_{out} is the amount of the mixture flowing out of the chamber per unit time, kg/sec; L_c' is the amount of the mixture withdrawn from the system per unit time, kg/sec; $x_c'^L$ is the weight fraction of component A in this mixture; G' is the amount of the mixture passing through the film along the flow path from the separating chamber inlet to a cross section at distance l from the inlet, kg/sec; x'^G is the weight fraction of component A in this mixture.

REFERENCES

1. N. N. Li, R. B. Long, and E. J. Henley, Ind. Eng. Chem., **57**, 18, 1965.

2. Chei I-Ch'u, Progress in Petrochemistry and Petroleum Refining [in Russian], izd. Khimiya, Moscow, 5–6, 73, 1965.

3. B. H. Sanders and C. Y. Choo, Petrol. Ref., **39**, 133, 1960.

4. R. C. Binning and F. E. James, Petrol. Ref., **37**, 214, 1958.

5. R. C. Binning, R. J. Lee, J. F. Jennings and E. C. Martin, Ind. Eng. Chem., **53**, 45, 1961.

6. J. W. Carter and B. Jagannadhaswamy, Brit. Chem. Eng., **9**, 523, 1964.

7. A. Michaels, R. F. Baddour, J. H. Bixler and C. Y. Choo, Ind. Eng. Chem., **1**, 14, 1962.

8. Yu. I. Dytnerskii, V. N. Golovin, N. V. Kochergin, M. N. Panfilov, and R. G. Kocharov, Abstr. Proc. Sci.-Techn. Conf. Moscow Mendeleev Chemical Engineering Inst., Moscow, 62, 1965.

9. Yu. I. Dytnerskii, V. N. Golovin, N. V. Kochergin, D. A. El'bert, V. B. Kvasha, V. M. Kireeva, and R. G. Kocharov, Abstr. Proc. Sci.-Techn. Conf. Moscow Mendeleev Chemical Engineering Inst., Moscow, 65, 1966.

10. A. A. Babenkov, A. N. Planovskii, and I. G. Martyushin, Abstr. Proc. Sci.-Techn. Conf. Moscow Inst. Chemical Machine Building, Moscow, 39, 1966.

11. Yu. I. Dytnerskii, V. N. Golovin, N. V. Kochergin, R. G. Kocharov, and L. I. Il'in, Trudy MKhTI im. D. I. Mendeleeva, Moscow, no. 51, 39, 1966.

7 December 1966