

CHEMICAL EQUIPMENT

PERVAPORATION SEPARATION OF HOMOGENEOUS LIQUID SYSTEMS

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At the present time, homogeneous liquid systems are separated by traditional methods: fractionation, adsorption, distillation, or liquid extraction. These methods, however, require either cumbersome equipment or a generous energy supply to achieve high-quality separation, or they (for example, extraction methods) are associated with the need for further treatment of the mixture being formed.

Use of membrane methods of separation makes it possible to solve many problems of rational utilization of natural resources and environmental preservation, for example, problems involving separation of homogeneous liquid mixtures, including the treatment of industrial waste water. These methods are, however, rather expensive.

The process of pervaporation^{*} permits replacement of traditional procedures and ensures high-quality separation with low expenditures for process realization [1].

The advantages of pervaporation technology are as follows: low energy consumption (during the pervaporation removal of high-boiling-point solvents, for example, styrene, ethyl benzene, and toluene, from industrial waste water, the outlays of thermal energy are seven times lower than for distillation [2]); low process temperature (no more than 60-80°C); this makes it possible to use low-grade heat; simplicity, compactness, and modular construction of the pervaporation units; this ensures their easy adaptation to the required production volumes; and ecological purity, since no auxiliary substances and reagents are required.

Analysis of specific examples of the use of pervaporation technology confirms its high economy. For production volumes to 1000 m³/day, expenditures for the pervaporation process are comparable with those for microfiltration processes and are significantly lower than those for adsorption or vaporization [1].

It cannot be stated, however, that pervaporation is widely used. The small volume of industrial implementation is explained by the absence of highly selective, productive, and at the same time, mechanically strong membranes; there are no procedures for selecting the membrane material for each specific case, and also no simple and sufficiently accurate mathematical models for calculating pervaporation units. No standard structural solutions that provide for a high rate of heat and mass exchange have been developed for equipment with a low hydraulic resistance.

The mechanism of mass transfer during pervaporation is usually subdivided into three successive stages:

- sorption of components from the liquid mixture by the surface of a selective polymeric membrane, i.e., a polymeric membrane possessing selective permeability;
- diffusion of the sorbate in the membrane polymer; and
- evaporation of the sorbate in the vapor phase from the opposing side of the membrane.

^{*}The term "pervaporation" is formed by the Latin prefix *per* (through, by means of) and the English term *evaporation*, i.e., literally means "by means of evaporation." In domestic literature, the term in question is usually translated as "evaporation through a membrane," but a variant reading arises as a result, since gas separation and membrane distillation also frequently apply to evaporation through a membrane. The term "pervaporation" is therefore proposed for a concise definition of the domain under consideration, and, precisely, processes involving the membrane separation of homogeneous liquid systems, which combine the solution and molecular diffusion of volatile components of a system in a selective nonporous membrane with their evaporation on its opposing side.

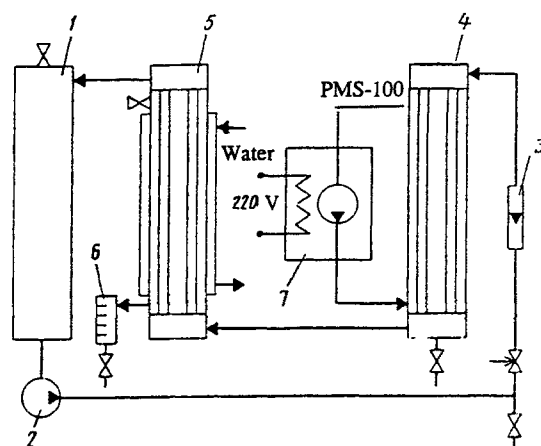


Fig. 1. Diagram of experimental unit: 1) storage tank; 2) pump; 3) rotameter; 4) heat exchanger; 5) membrane vessel; 6) permeate receiver; 7) thermostat.

The description of mass transfer during pervaporation is appreciably more complex than for other processes, for example, ultra- and microfiltration. The membrane cannot be selected merely on the basis of simple analysis of the sorptive capacity and diffusion coefficients of the individual components, since a strong influence of one component on sorption and the other on diffusion is observed [3]. In this connection, it is extremely difficult, and occasionally even impossible to predict the characteristics of the process, even when there are data on the sorption and diffusion of each component of the polymeric membrane.

The chemical nature and structure of the polymers used in preparing the membrane exert a decisive influence on the efficiency of the pervaporation process; selection of polymers for the membranes is therefore a key problem in the development of pervaporation vessels.

Considering the computed characteristics of pervaporation technology, pervaporation membranes are developed on the basis of polydimethyl vinylsiloxane, which is distinguished by some of the highest (among highly elastic polymers) diffusion and solubility coefficients of organic substances; the high energy of the siloxane bond, which is polar in nature; this supports a broad range of operating temperatures; a capacity to recycle in the initial state after swelling in the majority of organic solvents; this is required in treating organic solutions; and, stability in aggressive media; this makes it possible to use these membranes for the treatment of liquid systems with a pH ranging from 2 to 13.

Siloxane membranes are classed as nonporous diffusion membranes, i.e., they do not have through pores, and consequently are essentially insensitive to contamination and do not require regeneration. The process of diffusion permeability in these membranes can be interpreted qualitatively as the movement of sorbate molecules through walls of polymeric chains and vacancies. In a polymer, as in simple liquids, vacancies continuously vanish and form again under thermal fluctuations at a temperature above the glass-transition temperature. Diffusion takes place as a result of the movement of sorbate molecules from vacancy to vacancy under the thermodynamic-activity gradient of the sorbate and the joint action of a set of polymer units [4]. As a property of the membrane's ability to pass a substance, permeability is determined in this case by the capacity of the penetrating molecules to increase the number of moving polymer units, breaking the intermolecular bonds between them. In other words, a majority of the gases and liquids soluble in a membrane polymer may pass through this type of membrane.

The selection of membranes for pervaporation is a more difficult problem than, for example, the selection of membranes for ultra- or microfiltration. This is explained by the fact that for economically suitable use in separation processes, pervaporation membranes should, in addition to traditional requirements of high selectivity, productivity, and mechanical strength, successfully maintain contact with the organic solvents at elevated temperatures. As is apparent, these requirements are mutually exclusive. To increase the specific productivity of a membrane, for example, it is necessary to reduce its thickness; here, however, the mechanical strength of the membrane is lowered markedly.

In selecting the thickness and shape of developed membranes, therefore, it is necessary to consider the following:
 — selectivity of the separation of a liquid mixture is independent of membrane thickness [1];

TABLE 1

Substance	Impurity concentration, mg/liter	
	in waste water *	maximum allowable [7]
acetone	$\frac{100}{1,0}$	3,0
benzene	$\frac{14}{\text{traces}}$	0,5
xylene	$\frac{18,3}{0,14}$	0,5
methylene chloride	$\frac{200}{5,0}$	7,5
perchloroethylene	$\frac{7}{0,07}$	0,5
styrene	$\frac{72}{0,1}$	0,1
toluene	$\frac{36}{\text{traces}}$	0,5
trichloroethylene	$\frac{9,4}{\text{traces}}$	0,5
triethylamine	$\frac{10}{\text{traces}}$	2,0
phenol	$\frac{0,7}{\text{none}}$	0,001
chlorobenzene	$\frac{1,5}{\text{traces}}$	0,02
benzyl chloride	$\frac{3,2}{\text{none}}$	0,001
chlorotoluene	$\frac{5,3}{0,01}$	0,02
carbon tetrachloride	$\frac{60}{0,18}$	0,3
ethyl benzene	$\frac{3,6}{0,01}$	0,01

*In the initial mixture and after purification, respectively, in the numerator and denominator.

– as Romenburg [5] has demonstrated, the boundary diffusion layer, the portion of whose resistance in the overall resistance to mass transfer is directly proportional to the thickness of the membrane, i.e., the thicker the membrane, the higher the resistance of the boundary layer near its surface, exists near the surface of the membrane, and the tendency to produce ultrathin membranes is not always justified, therefore, in fabricating membranes on the basis of highly permeable polymers; and,

– a high specific surface of membrane elements is not required for low concentrations of one or several components of the liquid system, in connection with the fact that tubular and plane-parallel (filter-press type) membrane models are considered the most acceptable constructions [6].

After a series of experiments, we developed a production procedure, fabricated experimental batches of flat membranes 100-250 μm thick and tubular membranes 500-1000 μm thick, and prepared periodic and circulating types of experimental units for investigation of tubular and flat pervaporation membranes with a mass-exchange surface area of 0.25 and 0.08 m^2 , respectively. The principle of thermopervaporation during which vapors of substances passing through the membrane are condensed on the cold wall inside the membrane module is realized in the units.

A schematic diagram of the periodic type of experimental unit with a membrane having an effective surface area of 0.25 m² is shown in Fig. 1. The results of experiments on purifying waste waters from the production of styrene, polysulfone, and polycarbonate are presented in Table 1.

The data obtained confirmed the possibility of running pervaporation processes for the separation of azeotropic and thermally unstable mixtures of organic compounds, the concentration of organic solutions, and the purification of industrial waste waters from organic impurities.

It is established that the productivity of pervaporation units is determined to a large degree by the system's potential for tapping the flow of substances passing through the membrane (permeate). If vapors are not removed effectively from the side of the permeate, they are condensed on the external surface of the membrane, flowing along it as a film of condensate. This leads to the appearance of osmotic processes, the motive force of which is the difference in concentrations of the volatile component on both sides of the membrane. In this connection, no separation of mixture occurs in establishing equilibrium. The incomplete and untimely removal of vapors therefore degrades the characteristics of the process: productivity with respect to permeate and the quality of separation are lowered.

It is most acceptable to conduct the process under atmospheric pressure and maintain the effective temperature in the 50 ± 5°C range during treatment of water-organic mixtures, and at the level of the boiling point of the low-boiling-point component for treatment of mixtures of organic substances.

The creation of a vacuum in the vapor space of the membrane vessel could increase the productivity of the unit; this renders the formation and migration of vacancies difficult in the membrane, however, due to its internal deformations, and requires an increase in the temperature of the initial mixture in connection with the more vigorous evaporation of the sorbate. Moreover, a sharp increase in prices of energy-storage media has led to replacement of the "maximum productivity at any cost" strategy by the "minimum operating expenses for adequate production" development strategy in the area of membrane separation. It is therefore resolved to reject the captivating idea of vacuum treatment on the side of the permeate, not to mention that units, which have successfully operated without a pressure drop in the vapor space, are known [1].

Tubular pervaporation modules can be designed on the basis of a mathematical model for the process of pervaporation separation, which was developed in the National Technical University of Ukraine "Kiev Polytechnic Institute."

Three types of membrane models, which make it possible to implement the pervaporation process on an industrial scale, have been developed. A unit with an effective membrane-surface area of 20 m² and productivity of 15 m³/day has been implemented by the Production Union "Zarya" (Dzerzhinsk, Nizhegorodsk Oblast) for the purifying of waste waters from polycarbonate production of methylene chloride, phenol, and triethylamide. Another unit with a membrane-surface area of 5 m² and productivity of 1 m³/h has been installed at the plastic plant (Akatu Mangistausk Oblast, Kazakhstan) for purifying waste water from polysulfone production.

Designs have been developed for two commercial modular membrane units with effective membrane-surface areas of 20 and 100 m², which can be used to separate azeotropic and thermally unstable mixtures, concentrate solutions and recycle valuable organic substances in the production cycle.

Yet another promising area of application for pervaporation – separation of solid substances from organic solvents (for example, those used in the electronics industry) and crystalline solid substances from essential oils used in the foodstuff and pharmaceutical industry (for example, menthol from peppermint oil) – should be pointed out.

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