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Pervaporation: A Novel Process for Ethanol Separation using Fermentation

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Abstract:***Various separation processes were used in the chemical industry along with their corresponding separating agents. The separation processes play a critical role in various chemical process industries, including the removal of impurities from raw materials, purification of products, separation of recycle streams, and removal of contaminants from air and effluents. Hence it can be intensified by integrating of existing and new unit operations, it offers a huge increase in efficiency and controllability, thereby saving a lot of raw materials and energy, reducing waste production, increasing yield and quality and improving production safety. This review, deals on the development and implementation of small scale continuous processes and processing systems helping chemical industries to get more out of their processes*****.**

Keywords:- Pervaporation, Membrane, Separation, Ethanol, Fermentation.

1. Introduction

Separation processes play a significant role in process industry, including the removal of impurities from raw materials, purification of products, separation of recycle streams, and removal of contaminants from air and effluents. Overall separation processes account for 40-70 % of both capital and operating costs in process industry [1]. The proper application of separation processes can significantly reduce costs and increase profits. The various separation processes used in the chemical industry with separating agents are given in Table 1.

In general all processes used for the separation of fluid mixtures can be split into two categories: 1. Separation by equilibrium distribution, 2. Separation by differences in transport rates. The most common separation processes used on large scales in the industry are based on equilibrium distribution e.g. evaporation, distillation, extraction, adsorption, absorption. A first phase comprising a mixture to be separated is brought into contact with a second phase. After a certain time thermodynamic equilibrium is established between the two phases. That means both phases show the same temperature and all components have the same chemical potential in both phases. The analytical concentrations of a component in the two phases, however, may differ e.g. a component can be highly enriched in one phase and be depleted in the other one. If now the two phases are separated by appropriate means, the enriched component can be recovered usually by establishing a new equilibrium at a different temperature or pressure. If separation by differences in transport rates is to be achieved, an additional means is required. In some cases such a means is a membrane, separating two phases from each other. A driving force i.e. a gradient in pressure, concentration, temperature or electrical field is applied and has to be maintained over the membrane. Under the influence of this driving force, components from the mixture to be separated, held at a higher chemical potential, migrate through the membrane to the side of the lower chemical potential. The gradient in the chemical potential has to be maintained by continuous removal of the migrating components from the side of the lower chemical potential. If this is not done, equilibrium would be reached and no separation would occur, in most cases one of the phases would vanish [2].

A significant portion of the ethanol production process consists of the separation/dehydration stage. This has motivated the development of alternative processes to reduce its production costs. Economic analyses made through the internal return rate method have shown the economic feasibility of the membranes processes [3]. These processes allow the selective separation of components in a solution without thermal damage through the use of membranes [3], which are considered technically important in industries where they have been used for purification of aqueous streams, concentration and recovery of valuable products, production of potable water, concentration or removal of dissolved ions, splitting gas streams, removal or recovery of specific gases, and separation and concentration of liquid mixtures [4]. Among the different membrane processes are microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, gas separation, and the pervaporation process [5]. The last one can be considered an attractive process for the continuous removal of ethanol from fermentation wine, decreasing production costs and increasing its profitability [6-9].

Pervaporation is a separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a dense non-porous membrane as shown in Figure 1. During pervaporation, the feed mixture is in direct contact with one side of the membrane whereas the permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas and then condense. Pervaporation is unique among membrane separations, involving the liquid-vapor phase change to achieve the separation. The driving force for the mass transfer of permeants from the feed side to the permeate side of the membrane is a gradient in chemical potential, which is established by applying a difference in partial pressures of the permeants across the membrane. The difference in partial pressures can be created either by reducing the total pressure on the permeate side of the membrane by using a vacuum pump system or by sweeping an inert gas on the permeate side of the membrane [10].

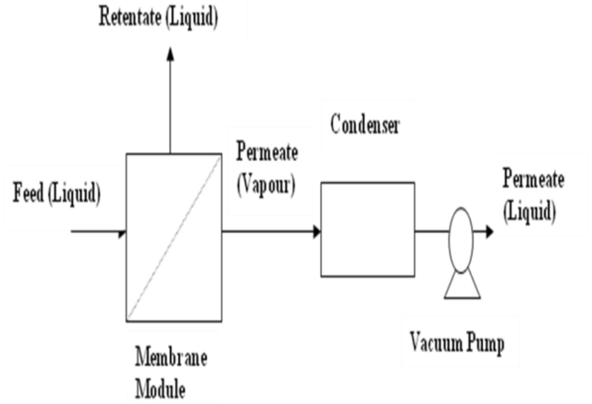

Fig. 1: Schematic diagram of pervaporation process.

2. PERVAPORATION REACTOR

The pervaporation reactor is as shown in Figure 2**,** specifically, the new technology for reaction and separation. It is rather difficult to predict the market potential of processes newly introduced on the market. However, in comparing investment costs, environmental aspects of pervaporation systems with those of conventional processes, it can be said that pervaporation reactor will play an important role in the chemical industry for new installations as well as for rehabilitation of existing plants. Techno-economic studies are showing that pervaporation reactors have good market potential. There are many examples where pervaporation reactors can reduce product costs by an important margin.

The most common reaction system studied for the application of pervaporation is an esterification reaction between an alcohol and an acid in the presence of a highly acidic catalyst (e.g., concentrated sulfuric acid).

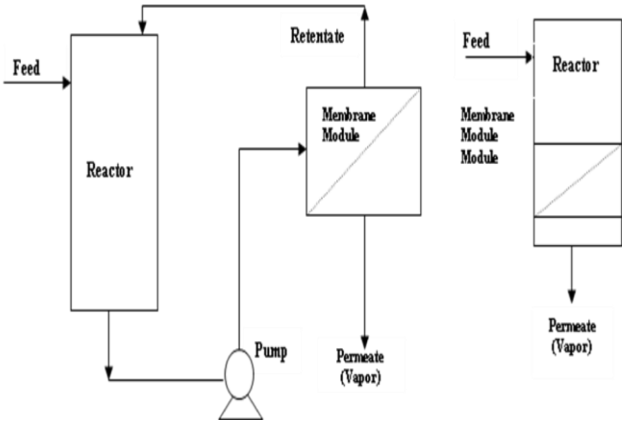

Fig. 2: Pervaporation Reactor (a) Ex-situ (b) In-situ.

3. CHARACTERISTICS OF PERVAPORATION

3.1. Molecular Flux

Molecular flux is the amount of a component permeated per unit area per unit time for a given membrane.

$$J_i = Q_i / (At) \quad (2)$$

3.2. Permselectivity

The performance of a given membrane can be expressed in terms of a parameter called permselectivity:

$$\alpha = (X_i^p X_j^p)/X_i^f X_j^f)$$

$$\alpha = (V_i^p \rho_i^p / V_j^f \rho_j^f) /(V_i^f \rho_i^f / V_j^f \rho_j^f)$$

Assuming the density of the components in the feed is the same, then:

$$\alpha = (V_i^p / V_j^f) /(V_i^f / V_j^f)$$

3.3. Permeability Coefficient

The molecular flux for pervaporation across a membrane can be related to the permeability coefficient by:

$$J_i = -P_i \Delta P/L$$

Or

$$J_i = k \Delta P/L$$

Here, $\Delta P = P_1 - P_2$ and $P_1 = P_i^o X_{r,i,}\gamma_i$ & $P_2 = P Y_{p,i,}$

Therefore,

$$\Delta P = (P_i^o X_i - P Y_{p,i})$$

Equation 6 becomes,

$$J_i = -P_i(P_i^o X_{r,i} - P Y_{p,i})/L$$

P_i=-J_i L(($P_i^o X_{r,i\,,\gamma i}$ - P $Y_{p,i}$)

3.4. Membrane

The membrane is the most important part of pervaporation-it is where the phenomenon of separation is taking place through a solution-diffusion mechanism. As such, the membrane must satisfy three important requirements: productivity, selectivity, and stability [11]

3.5. Membrane productivity

It is characterized by permeation flux (J), which is a measure of the quantity of a component that permeates through a specific area of membrane in a given unit of time [12].

3.6. Membrane selectivity

The ability to permeate a specific compound through the membrane. It is expressed by a separation factor (α), which is a dimensionless quantity dependent on the concentration of the permeate component [13].

3.7. Membrane stability

The ability of a membrane to maintain both the permeability and selectivity under specific system conditions for an extended period of time [11]. In terms of their characteristics, the membranes used for pervaporation are made from both asymmetric and composite non-porous materials and present high productivity, good selectivity, and long-termstability [14]. Thus, the most commonly reported membrane for the recovery of biofuels is PDMS [15], a hydrophobic membrane selective for alcohols, such as ethanol and butanol, and VOCs from dilute aqueous solutions due to their elastomeric characteristics that gives excellent film-forming ability, thermal stability, and chemical and physiological inertness [16].

4. PERVAPORATION APPLICATIONS

4.1. Ethanol Production and Separation

Pervaporation has proved to be a straight forward technique for in-situ alcohol recovery from fermentation broth [17-19]. It has been proven that pervaporation is a more energy efficient technique for ethanol separation.

4.2. Butanol Production and Separation

Pervaporation reactor has been studied to separate butanol from an aqueous solution [20]. A specially designed and manufactured cell was used to separate the butanol from butanol/water solutions of different butanol concentrations (6-8-11-16-20-50) g/l. 250 cm^3 butanol mixture at 33^OC was used to feed the cell, while the pressure of permeation side was about ∼ 0 bar. Results revealed that butanol concentration changes non-linearly during the first 3 h, and then proceeds linearly. The percentage of butanol removal increases with increasing feed concentration. The permeability of the used membrane was determined experimentally. A resistance in series model was used to simulate the pervaporation step. The butanol concentration in the feed during the pervaporation step was predicted by using the developed model. There is a fair agreement between butanol concentration in feeding tank of pervaporation cell both experimentally and predicted from the developed model.

4.3. Dehydration of solvents

Dehydration of *n*-butanol has been carried out using several silica membranes [21]. Typical values for the initial water flux and selectivity are in the range of 2–3 $kgm^{-2}\ h^{-1}$ and 500–1200, respectively. The water permeance decreases with time. The selectivity also appears to decrease with time, although this effect is less apparent. Interactions of solvents with the silica material are expected to be more pronounced when the dipole moment of the solvent molecules is larger. Dimethylformamide (DMF) is an example of a solvent with an exceptionally high dipole moment. Dehydration of DMF has been carried out using several silica membranes [21]. A decline of the water permeance is observed with time.

4.4. Waste water treatment

Pervaporation has been considered as an alternative technology for removal of volatile organic compounds from contaminated water. The contaminated water may be an industrial process water, groundwater or leachate. For water treatment applications, the membrane is made of an organophilic polymer such as silicone rubber, which exhibits good permeability for the organic compounds while allowing very limited passage of water. Most organic compounds are concentrated in the permeate by orders of magnitude compared to the aqueous waste. The organics and some water which passes through the membrane are condensed; the condensed permeate often separates into an aqueous and an organic phase, offering industrial applications the possibility of recovering the organic fraction.

4.5. Refining of alcoholic beverages

The pervaporation experiments were carried out with samples having 5.8 - 43.1 wt% of alcohol contents by using PDMS (polydimethylsiloxane) 1060, 1070 and DS-7 pervaporation membrane. Results showed that the removal ratio of impurities such as aldehydes, ester and sulfides in the process of using PDMS membrane was higher than using DS-7 membrane and hence is more efficient. In this study, downstream pressure was the most important factor affecting the performance of pervaporation. Depending upon the high or low downstream pressure, the overall results were remarkably different.

4.6. Improving natural flavors

An integrated bioprocess (IBP) for production and recovery of de novo synthesized aroma compounds was carried out by interlinking a pervaporation membrane module with a producing bioreactor. The main aroma products of the fungus Ceratocystis moniliformis were ethyl acetate, propyl acetate, isobutyl acetate, isoamyl acetate, citronellol and geraniol. In situ product removal (ISPR) using pervaporation leads to decreased product concentrations in the bioreactor and increased microbial growth rates. As a result, by circumventing inhibiting product concentrations and thus intensifying aroma production, total yield of aroma compounds produced is higher in an IBP compared with batch cultivation. In addition, permeates obtained from pervaporation consist of highly enriched mixtures of produced flavors and fragrances [22]. Scientists at the Dutch Agro technology and Food Innovatives (A&F) institute, a unit of Wageningen University, are behind a drive to provide flavor houses with natural foodstuff flavors of high concentrations and fresh authentic character, using a flavor isolation process that has a high selectivity towards specific volatile compounds.

4.7. Aroma recovery

The development of hollow fiber pervaporation module is a breakthrough and gives additional advantages. The pervaporation equipment can be built more compact, a higher concentrated aroma can be produced, pressure drops are low and investment costs in the membrane module are significantly reduced. The technology is especially of interest for aroma and flavor producing companies and canned food processing industries [23]. Main advantages of aroma recovery with pervaporation are: (a) mild processing conditions, (b) high concentration of aroma, (c) no additional chemical required, (d) low energy consumption, (e) flexible adjustable equipment through modular design, and (f) easy process operation.

4.8. Petroleum refining and chemical processing plants

Pervaporation is particularly useful for separating aromatics from non-aromatics in petroleum refining and chemical processing plants. These membranes have the added advantage of being chemically and mechanically robust; they will not deteriorate or break when placed in service. The energy used for separation is decreased and economical hybrid distillation-membrane separation processes are made possible with pervaporation of hydrocarbon mixtures utilizing specially formulated blends of rubbery polymer. There are several organic/organic mixtures which could be separated by pervaporation: alcohols/ethers (methanol//MTBE, ethanol/ETBE), aromatics/paraffins (benzene/hexane), branched hydrocarbons from n-paraffins (isooctane/hexane), olefins/paraffins (pentene/pentane), isomeric mixtures (xylenes), chlorinated hydrocarbons from hydrocarbons (chloroform from hexane), purification of dilute streams (isopropyl alcohol from heptane/hexane) [24].

4.9. Fuel application

Purification of ethanol to fuel specifications is an energy intensive process. The current industrial technology for ethanol recovery and purification is distillation of the filtered fermentation broth, in which the ethanol is concentrated from an initial concentration of approx. 10 vol% to 95 vol%. For fuel applications the water content of the bioethanol must be further reduced to < 0.1 wt%. Pervaporation is the most suitable technique for this 'deep' dehydration [25]. New technological developments for dehydration include the application of high temperature membrane separation processes for pervaporation or vapour permeation, which can be integrated with the distillation process.

4.10. Separation of water-organic mixtures

Pervaporation lead to great technical and economical benefits in the separation of butanol from an ABE process. The major advantages of pervaporation in this process are the possibilities for direct product capture, where the membrane operating conditions are similar to the fermentation conditions. The membranes are also modular in design making scale-up straightforward [26] Extensive research has been carried out for other organic acid and alcohol systems like benzoic acid and ethanol system etc, but the acetic acid, lactic acid, propionic acid with ethanol, n-butanol, iso-propanol reaction system have undergone very limited research despite its extensive applications in industry. Therefore the present work is focused on this system [26].

CONCLUSION

Pervaporation reactor is a combination of reactor with pervaporation system especially suitable for equilibrium controlled reactions such as esterification reactions. In comparing investment costs and environmental aspects of pervaporation reactor systems with those of the conventional processes, pervaporation reactor can play an important role in the chemical industry for new installations. Techno-economic feasibilities show that pervaporation reactors have good market potential. This review will be useful for the design of pervaporation reactor for similar kind of reactions.

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