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# Separation of methanol–*n*-butyl acetate mixtures by pervaporation: Potential of 10 commercial membranes

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The transesterification reaction to produce methanol and butyl acetate has great interest in the chemical industry. The separation of these two compounds from the reaction media increases the productivity, thus, a hybrid configuration composed of reaction–pervaporation is of interest. In this work, 10 commercial specialty membranes (PolyAn and Sulzer Pervap membranes) have been studied in a pervaporation setup at three temperatures (30, 40 and 50 °C) and a feed concentration ranging between 20 and 80 mol% methanol/butyl acetate in order to determine their performance in terms of permeance, selectivity and the McCabe–Thiele separation diagram. From the results, it can be observed that most of the membranes are butyl acetate selective, with selectivities up to 307 and permeances of butyl acetate up to about 80,000 GPU. In general, an increase in temperature decreases the permeance of butyl acetate through the PolyAn membranes and it has a dramatic effect on the Pervap 1201 membrane since the selectivity to butyl acetate decays from 300 at 30 °C to around 0.2 at 50 °C. The Pervap 2255–50 membrane presents an increase of selectivity as the temperature increases. On this basis the potential of developing a pervaporation membrane reactor for production of butyl acetate by transesterification is assessed.

## 1. Introduction

Transesterification reactions are equilibrium-limited reactions in which an ester and an alcohol are produced, involving a post-reaction organic–organic separation. The heterogeneously catalyzed transesterification reaction between butanol and methyl acetate to produce butyl acetate and methanol is a key reaction in the chemical industry:

$$\frac{CH_3COOCH_3}{\text{(methylacetate)}}+\frac{CH_3(CH_2)_3OH}{\text{(butanol)}}\leftrightarrow\frac{CH_3COO(CH_2)_3CH_3}{\text{(butylacetate)}}+\frac{CH_3OH}{\text{(methanol)}}$$

*n*-Butyl acetate is an important solvent in chemical industry, mainly used in paint and coating manufacture and the lacquer industry. Methyl acetate is a by-product of the poly-(vinyl)-alcohol production and has to be converted to methanol, which is a feedstock of the poly-(vinyl)-alcohol production among other applications [1].

The transesterification reaction is reversible and the equilibrium constant is close to unity, with a low reaction rate and complex phase equilibrium behavior [2,3]. A traditional separation based on phase equilibrium such as distillation after the reaction step involves the formation of two azeotropes: methanol–methyl acetate and butanol–butyl acetate. Thus, the purification of products is not straightforward and effective strategies have to be developed. Jimenez and Costa-Lopez [4] developed a novel process based on reactive and extractive distillation using *o*-xylene as entrainer in order to synthesize, design and study the dynamic behavior for the azeotropic separation. Reactive distillation has been also proposed by Steinigeweg and Gmehling [1] as a promising process in combination with pervaporation which separates the azeotropic mixture methyl acetate–methanol. Reactive distillation is the combination of reaction and distillation within one unit operation. The direct removal of the products or intermediates from the reactive section of the column by distillation, which is especially interesting for equilibrium limited reactions, leads to higher conversions and selectivities [5]. However, the presence of the two binary azeotropes makes it necessary to combine the reactive distillation with other unit operations [1] or to search for alternative separation processes due to the complex design and synthesis resulting from the interaction of chemical reaction and distillation [6]. On the other hand, pervaporation is a promising alternative to conventional energy-intensive technologies for being more economical, safe, and ecofriendly, and for having interesting energetic aspects, which justifies the development of hybrid processes such as reactive distillation–pervaporation processes. However, inclusion of pervaporation-based hybrid processes in the industry has not gone very far due to the lack of methodology for design and optimization of those processes and the fact that commercially

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available polymeric membranes are not generally applicable to organic solutions because of insufficient chemical and temperature stability. Nevertheless, the huge market in the chemical and petrochemical industries justifies the importance of the separation of organic–organic mixtures and it will surely be one of the focuses of the future pervaporation research [7].

The use of pervaporation to separate azeotropic mixtures is technically viable due to the intrinsic performance of this technology. Pervaporation is a separation technique based on the partial vaporization of compounds through a (commonly) non-porous membrane (dense membrane). The membrane acts as a selective barrier between the two phases, the liquid feed solution and the vapor phase permeate, and the driving force for the separation is the difference in the partial pressures of the components on the two sides of the membrane. The selectivity of the separation is given by different transport rates of the molecules through the membrane as a result of different solubilities and diffusivities of the components. Thus, the presence of azeotropes does not affect the efficiency of the separation. An approach still under development is to use pervaporation directly for the separation of the resulting products or by-products in the reactor. In this case, pervaporation is integrated with a chemical reactor [7]. The most used membranes are by far hydrophilic membranes for removal of water from the reaction medium present in esterification reactions. The idea of using a pervaporation module to remove water from an esterification reaction was suggested for the first time already in 1988 by Kita et al. [8]. Since then, many studies are focused on water–organic separations (e.g. [9–15]). However, the separation of organic–organic mixtures is still scarce in the literature [16–18]. For organic–organic separation polymeric membranes are mainly chosen on the basis of relative solubility parameter of the organics and the membranes [19], although for the separation of a smaller amount of methanol from ethers like MTBE, hydrophilic membranes are used [20]. Apart from commercial cellulose acetate membranes [21] various polyvinyl alcohol (PVOH) membranes [22] and acrylic copolymers [23,24] have also been reported in recent years for pervaporative removal of methanol from MTBE or other similar ethers. Furthermore, there is only one industrial application of pervaporation using organo-selective membranes for the continuous removal of methanol during the synthesis of a methyl ester by Sulzer Chemtech [25]. This great achievement opens a new realistic field of research since removal of methanol from organic–organic mixtures is nowadays an energetic-intensive process when azeotropic mixtures are formed.

Organic–organic separations are still a challenge but also an opportunity to integrate pervaporation and reaction in a wide range of applications in the chemical industry. One configuration proposed by Lipnizki et al. [26] is based on removal of products in order to improve the productivity of the reactor so that the overall process can be considered to be integrated and optimized as a hybrid process. This hybrid process overcomes the inhibition of the chemical equilibrium of the process and allows using heat of the chemical reaction to increase the efficiency of the pervaporation process. The only requirement to be competitive with conventional separation processes is a high permeability for the target compound, this is, high production and high selectivity.

In this work, the mixture to be studied is composed of methanol and butyl acetate as a first step in the research to find the optimal membrane to separate these two compounds. Selective removal of methanol or butyl acetate is aimed in order to shift the reaction equilibrium to a higher product yield, according to the principle of Le Châtelier-Braun. Several commercial specialty membranes with different nature are used at three different temperatures (30, 40 and 50 °C) and a feed concentration ranging from around 20 to 80 mol% in order to obtain a general view of the real possibilities to apply this technology in a short term. The mixture 50–50 mol% methanol/butyl acetate is very representative of a real scenario where the hybrid reactor-pervaporation can be used instead of a later separation of products by means of reactive or extractive distillation. Avoiding the use of distillation is a challenging approach but it can be afforded if an appropriate separation membrane under optimal conditions is found.

## 2. Methods and materials

### 2.1. Chemicals and membranes

Methanol ( > 99.8%) and butyl acetate ( > 99%) were supplied by Sigma Aldrich (France) and Chem-Lab (Belgium), respectively, and were used without further purification. Several commercial membranes were used in this study. The trade name and the supplier are shown in Table 1. All the membranes are designed for organic–organic separations.

According to the supplier, the PolyAn membranes are composite membranes produced by using PolyAn's Molecular Surface Engineering technology [27]. A commercially available polyacrylonitrile (PAN) ultrafiltration membrane provides the support and a thin, defect-free, cross-linked polymeric functional matrix is covalently anchored in the separation layer of the support using the pore-filling concept. The thickness of the selective functional polymer layer is 1–3 μm. Regarding the Sulzer Pervap membranes, the Pervap 1201 is a polyvinyl alcohol (PVA) membrane and the Pervap 2055–50 has a pore-free separation layer comprising a polymer mixture (at least two polymer components such as PVA) for separating simple alcohols and water from mixtures thereof with other organic fluids [28]. Thus, both kinds

**Table 1**
Commercial membranes tested for methanol–butyl acetate separation.

| Membrane | Supplier |
|---|---|
| Typ M1* | PolyAn GmbH, Germany |
| Typ M2* | PolyAn GmbH, Germany |
| Pol AL M1* | PolyAn GmbH, Germany |
| Pol AL M2* | PolyAn GmbH, Germany |
| Pol AR M1 | PolyAn GmbH, Germany |
| Pol AR M2 | PolyAn GmbH, Germany |
| Pol OL M1 | PolyAn GmbH, Germany |
| Pol OL M2 | PolyAn GmbH, Germany |
| Pervap 1201 | Sulzer Chemtech, Switzerland |
| Pervap 2255–50* | Sulzer Chemtech, Switzerland |

* Alcohol selective membranes.

**Table 2**
Increase of weight after immersion of membranes in 50/50 (mol%) methanol-butyl acetate solution.

| Membrane | Weight before immersion (g) | Weight after inmmersion (g) | % weight increase |
|---|---|---|---|
| Typ M1 | 0.4174 | 0.5798 | 38.9 |
| Typ M2 | 0.4230 | 0.6119 | 44.7 |
| Pol AL M1 | 0.3848 | 0.5400 | 40.3 |
| Pol AL M2 | 0.4438 | 0.6092 | 37.3 |
| Pol AR M1 | 0.3848 | 0.5467 | 42.1 |
| Pol AR M2 | 0.3747 | 0.5133 | 37.0 |
| Pol OL M1 | 0.3707 | 0.5302 | 43.0 |
| Pol OL M2 | 0.3815 | 0.5756 | 50.9 |
| Pervap 1201 | 0.3640 | 0.5426 | 49.1 |
| Pervap 2255–50 | 0.3122 | 0.4816 | 54.3 |