Membrane separation of ABE products from fermentation broths

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Introduction

Clostridium acetobutylicum is a bacterial species that ferments a variety of carbohydrates to a mixture of organic solvents (acetone, butanol and ethanol). Known as ABE fermentation, the process has seen renewed attention for the production of butanol, because of its physical properties, exhibiting wide applications in the energy (biofuels) and chemical industries. Currently, the focus is on the use of renewable raw materials including low-cost lignocellulosic residues from agricultural and agro-industrial processes.

Batch fermentation is the most studied fermentation mode due to simple operation and low risk of contamination (Qureshi, Saha, and Cotta 2007). To keep toxic levels due to butanol (>13 g/L) low to the fermenting microbes, in situ product removal has been suggested to alleviate product inhibition (Li et al. 2022). At the same time, it would reduce cost production of biobutanol, making it possible to increase the production rate by a factor of 3-9 as compared with that attained in the conventional process (Borisov et al. 2014). However, for ABE process to become commercially viable, higher product yields and concentrations are required. In addition, due to the non-ideal behaviour of the mixture, some products (ethanol and n-butanol) form azeotropes with water, and the n-butanol/water system is partially miscible and thus require multiple distillation columns, a decanter to separate a two-phase stream and a substantial amount of energy to separate each solvent.

Different strategies have been studied for the biobutanol produced from biomass, such as the use of new engineered *Clostridium* strains to selectively improve butanol production, the optimization of the fermentation parameters, etc. One important bottleneck of biobutanol production is the low product concentration in the fermentation broth upon completion of ABE fermentation (<1.8 wt%) (Li et al. 2021). Hence, it is necessary to increase the bio-alcohols production efficiency in order to improve the economic and environmental sustainability of the process (Romero-Izquierdo et al. 2021). Pervaporation (PV) is considered for the downstream process as an economic and safe option for organic product removal/ recovery. PV is a well-known technology with many advantages for the removal of organics, in addition to not affecting microorganisms and avoiding losses of nutrients and substrates. Nevertheless, PV efficiency might be limited by the membrane performance. Thus, the development and understanding of the performance of innovative membranes, as well as the application in real fermentation mixtures is important to meet industrial competitiveness. In this work, the performance of a custom-made thin film membrane was compared to a commercially available pervaporation membrane using synthetic and real feed fermentation mixtures in order to understand the major barriers that hinder the separation.

Materials and Methods

An organophilic commercial membrane made of polyether block amide (PEBA) supplied by Pervatech was used as benchmark for the synthetic membranes. The polymeric synthetic membranes prepared in this work were fabricated by the temperature-induced phase-inversion technique (TIPS) and characterized as in our previous work (Arregoitia-Sarabia et al. 2020). The first feed mixture consisted of a synthetic ABE mixture with a weight ratio of 3:6:1. A second synthetic mixture contained ABE and acids (acetic acid and butyric acid) as in literature. A third feed mixture proceeding from a real broth from the fermentation of glucose by *C. acetobutylicum* DSM 792 (DSMZ, Braunschweig, Germany) was used. The conversion was accomplished by pH-controlled batch fermentation in a defined medium to set the parameters for the fermentation of complex biomass into butanol. Fermentation performance was assessed through: HPLC for glucose, acid and solvent quantification; pH monitoring; optical density and quantification of the produced biogas. The PV separation of the membranes was carried out by using a lab scale PV unit. For the testing the membrane separation performance with the real ABE fermentation broth, the implementation of a pre-treatment was necessary to make sure no organic loading was within the feed to prevent fouling of the PV membrane. A vacuum filtration device with a 0.22 µm membrane was used. Sample characterization was done by gas and ionic chromatography, pH control. The PV performance was evaluated in terms of permeate flux J, separation factor β and pervaporation separation index (PSI).

Results

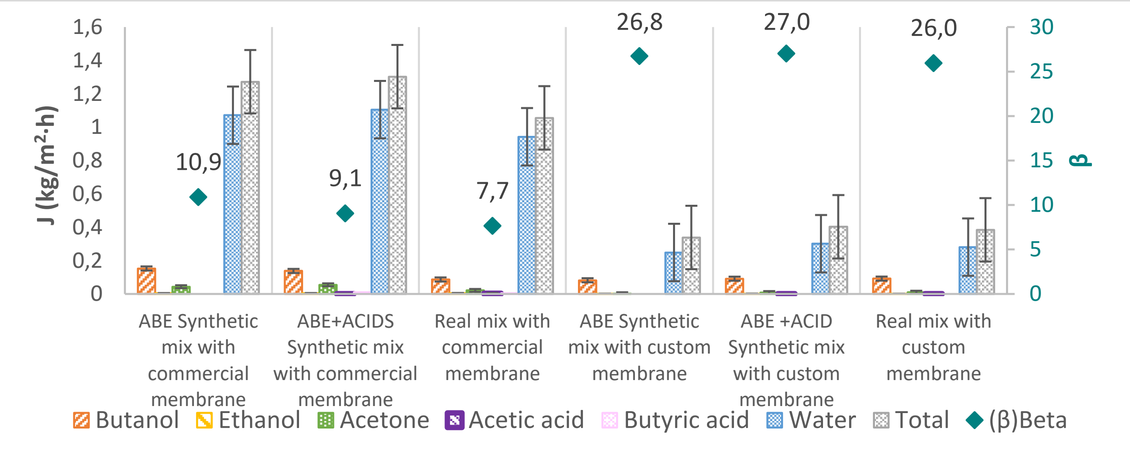

Figure 1. Flux performance and separation factor (β) of PV membranes in different feed compositions

When the synthetic mixtures were used as a feed stream, both commercial and custom-made membranes were selective to organics over water (Figure 1). Both membranes, commercial and custom-made, presented an acceptable butanol flux, slightly higher with the commercial membrane. But the most significant difference was seen in the water flux, which was much higher for the commercial membrane, so that the selectivity of the membrane towards butanol, expressed as a separation factor, was clearly higher for the custom-made membrane (27) than for the commercial membrane (9.1). When comparing the separation performance using the mixture from the fermentation broth, the following was observed: (a) working with the commercial membrane, the permeation fluxes decreased compared to those obtained with the synthetic mixtures, as well as the separation factor (7.7); (b) working with the custom-made membrane, fluxes and separation factor (26) were very similar to those previously obtained with the synthetic mixture. Both membranes produced similar butanol fluxes, but again the water flux was much lower with the custom-made membrane. Thus, using the PSI index to quantify the separation performance with the mixture from the fermentation broth, the advantage of our custom-made membrane (PSI=9.5) over the commercial membrane (PSI=7.1) is evident.

Conclusions

Organic compounds were effectively removed from the broth obtained from glucose fermentation by *C. acetobutylicum* using pervaporation separation. Performance of commercial and custom-made PV membranes were tested in synthetic feed mixtures and compared with real fermentation feed. For the custom-made membranes, the pervaporation tests showed better separation in terms of separation factor (β) although a lower overall flux was obtained. Thus, PV limitations rely mainly on the membrane used. Although commercial and custom-made membranes produced similar butanol fluxes, the water flux was lower with the later, resulting in a higher butanol content in the permeate stream, which facilitates subsequent distillation separation steps.

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