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Novel hybrid process for bio-butanol recovery: Thermopervaporation with porous condenser assisted by phase separation

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ABSTRACT

Novel hybrid process based on thermopervaporation (TPV) assisted by liquid-liquid phase separation in liquid permeate is proposed. The key component of the proposed process is a new concept of the TPV process with a porous condenser (TPV-PC). The TPV-PC approach makes it possible: i) to use the permeate as a coolant, ii) to solve the problem of the air-gap flooding and iii) to reduce the air-gap width below 1 mm. Limited miscibility of the water-butanol system leads to the phase separation of the permeate solution. Water-enriched phase from the decanter is used as the coolant in TPV-PC. The equilibrium vapor pressure remains constant value in the whole range of phase separation of butanol-water mixture providing the constant value of driving force of the TPV-PC.

The novel hybrid process was studied for separation of multicomponent model mixtures and the centrifuged real ABE fermentation broth. Four commercial pervaporation membranes were benchmarked and the MDK-3 membrane (Vladipor, Russia) was selected for further process investigation because of the highest pervaporation separation index. The effect of feed composition and temperature on the recovery and concentration of ABE components as well as membrane fouling was investigated. To mitigate the inhibiting effect of butanol and its concentration in the permeate above the phase separation point the proposed hybrid process should be performed at temperatures above 50 °C if the coolant/permeate temperature is 10 °C. For instance, at feed temperature of 60 °C, the degree of recovery of ABE components was nearly 80%, and concentration of butanol in the fermentation broth was decreases below 0.5 wt% from the initial value of 1.6 wt%. This hybrid process is expected to be also applied for other liquid mixtures treatment if and when liquid-liquid phase separation occurs in the permeate.

1. Introduction

Butanol and its derivatives are bulk chemicals which are widely used as solvents and feedstock materials in chemical, petrochemical, paint, and coating industries (global market of butanol exceeds 5 bln USD) [1–3]. Nowadays, great interest is focused on butanol produced by the fermentation process as the second-generation fuel for internal combustion engines due to its renewable origin and attractive energy density (~29.2 MJ/l) and as a promising feedstock for biorefineries [3–6]. Noteworthy is that, initially, butanol was primarily produced via the industrial fermentation process. In the 1960s, due to evident progress in petrochemistry and increased cost of biomass feedstock traditionally used for this process, biobutanol was replaced with synthetic butanol. By the 1980s, only few biobutanol plants have survived in the USSR, China, and South Africa [4] and, by the late 1990s, the last biobutanol production has been stopped in China [7]. However, in the late 2000 s, the interest to bio-based butanol has been revived, and demo and industrial scale fermentation processes have been launched worldwide.

The state-of-the-art process for biobutanol production is concerned with acetone-butanol-ethanol (ABE) fermentation but this process has certain drawbacks which hinder its wider industrial implementation: (i) yeast fermentation is the two-stage and low-rate process (conversion of carbohydrates into organic acids and their derivatives and further transformation to primary products such as acetone, butanol, and ethanol); (ii) fermentation products inhibit the activity of microorganisms at their low concentration level (e.g., from ~0.5 g/l); (iii) due to low concentrations of organic components which should be removed from the broth, the traditional separation methods such as distillation become less economically favorable; (iv) typical ABE yeasts are thermally-sensible and cannot preserve their activity in the separation mixture at temperatures above ~ 40 °C.

To overcome these limitations, the fermentation process was modified by the use of two (or more) reactors with different cell cultures which provide a stepwise conversion of the feedstock in the

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continuous mode. Microorganisms responsible for the fermentation of organic acids can be retained in the first reactor by separation from the liquor (e.g., centrifugation, decantation, filtration) or by immobilization on insoluble supports [8,9]. As a result, the duration of the continuous fermentation process can be extended up to 1250 h; the yield and level of butanol production are equal to 88% and 6.1*g*/l h, respectively. Hence, this approach can be considered as a marked improvement over the traditional batch mode of the ABE fermentation (30 h, 30%, and 0.4*g*/l h, respectively) [9,10].

Nowadays, conversion of raw materials can be appreciably increased by the use of two main approaches which mitigate the effect of yeast inhibition by fermentation products: the use of strains which are resistant to organic solvents and a continuous removal of organic compounds from the fermentation broth [11–19]. Among different separation techniques for biobutanol recovery, separation of dilute aqueous solutions of butanol by phase separation offers additional advantages related to the enrichment of the vapor phase by the organic component; for example, for 1 wt% butanol solution at 50 °C, the phase transition separation factor is equal to 26.8 [15]. Since dense hydrophobic membranes can provide additional separation via sorptional selectivity, great attention has been focused on vacuum organophilic pervaporation which is a single-stage process for the continuous treatment of the fermentation broth under mild conditions [19–35]. In particular, according to [19], energy consumption at the separation stage can be reduced by 50% when, prior to the conventional distillation, butanol is preliminarily concentrated from 0.5 up to 9.0 wt% by the organophilic pervaporation.

In contrast to optimistic experimental results on the model mixtures, the process of vacuum pervaporation can hardly be effectively used for the treatment of the real fermentation broths due to the presence of non-condensable gasses such as carbon dioxide and hydrogen (e.g., 1 mol of CO_2 is produced with 1 mol of BuOH). Hence, this process requires a continuous maintenance of vacuum at the required level and, as a result, the operation cost dramatically increases. Therefore, we have recently proposed a new thermopervaporation (TPV) concept by using the first generation of polymers with intrinsic microporosity, for example, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) that provides an effective recovery of butanol from its aqueous solutions at atmospheric pressure [36–42]. As was shown later, two other commercial silicon-based membranes (Pervap 4060 and Pervatech) can also be used for the butanol recovery via the TPV process [40].

Thermally driven membrane processes with the air gap configuration such as membrane distillation and TPV are known to have certain limitations related to their module design in order to avoid the flood of the chamber between the membrane in contact with the feed and the cooling plate. In the traditional TPV module, the condensed liquid travels along the cooling surface under the action of gravity force and is accumulated in the bottom part of the air-gap compartment. Long-chain linear alcohols such as 1-butanol demonstrate surface-active properties such as a long pathway of the liquid in the air-gap, which may provide the development of a continuous liquid phase between the membrane and the cooling surface. As a result, selectivity and transport parameters of the process can be dramatically deteriorated. For example, according to [39], the air gap width in the TPV scheme should not be lower than 2.5 mm in order to prevent a partial filling of the air gap by the liquid permeate.

Recently, a proof of principle of new the TPV process with a porous condenser (TPV-PC) has been proposed, and this approach makes it possible to solve the problem of the air-gap flooding and to reduce the air-gap width below 1 mm [36,41]. As a result, the permeate vapors are condensed on the cooled surface of the porous condenser and can be removed by evacuation from the air-gap through the pores due to the lower pressure in the coolant circuit in the gas part. The porous condenser offers a simplified design of the membrane module (see Fig. 2) because, in this case, in contrast to the classical TPV with a non-porous cooling surface (see Fig. 1), no liquid outlet for the air gap is required.

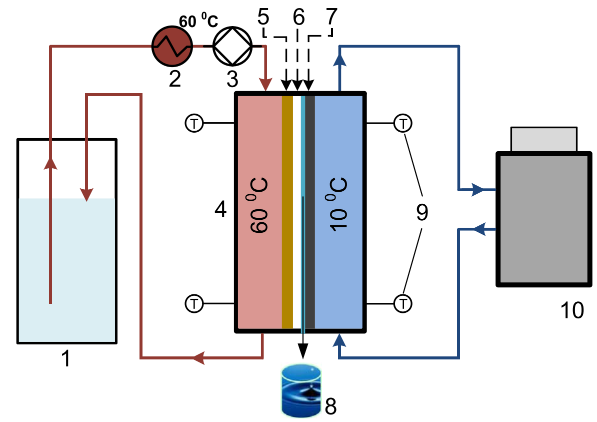

Fig. 1. A general sketch of the thermopervaporation lab scale setup: 1 – feed tank, 2 – heat exchanger, 3 – pump, 4 – TPV module, 5 – membrane, 6 – air gap, 7 – cooling plate, 8 – permeate collector, 9 – temperature detectors, 10 – heat exchanger with coolant.

When butanol concentration is higher than ~7.5 wt%, limited miscibility of the water-butanol system leads to the phase separation of the permeate solution. Noteworthy is that the equilibrium vapor pressure remains constant value in the whole range of phase separation of butanol-water mixture (~7.5–80 wt%) [42]. Therefore, the water-enriched equilibrium solution containing ~7.5 wt% of butanol can be directly used as a coolant which provides the same driving force during the separation process since the increase of butanol content in permeate does not change its equilibrium vapor pressure. Organic components are accumulated in the organics-enriched equilibrium solution, which can be separated in the decanter for further fractionation and purification using conventional industrial separation technologies such as distillation. Moreover, the water-enriched phase seems to be also attractive for the distillation separation due to the higher content of butanol and other organics compared to fermbroth. Thus, the TPV-PC process can be considered as a promising separation step which might be integrated into the existing ABE fermentation process. However, systematic studies on recovery of organic compounds from aqueous media in the membrane modules of this type are not currently presented in the literature.

The goal of this work was to study the proposed novel hybrid process for biobutanol recovery/concentration from model and real ABE fermentation broth. For benchmarking, four commercial silicon-based membranes were screened and, for further detailed study, the membrane with the best performance was selected.

2. Experimental

2.1. Membranes

In this study, four poly(dimethylsiloxane) (PDMS) based commercial flat sheet membranes were used: Pervap™ 4060 (Sulzer Chemtech, Switzerland), Pervatech (the PDMS membrane, Pervatech, the Netherlands), POL_OR_M2 (PolyAn GmbH, Germany), and MDK-3 (Vladipor, Russia).

2.2. Separation mixtures

All solutions were prepared from organic solvents (graded as chemically pure substances) by weighing. As model fermentation broths, we used the binary solution of 1-butanol in water (1.0–2.0 wt%) and the four-component acetone-butanol-ethanol solution in water (0.76, 1.6, and 0.3 wt%).

Real fermentation broths were prepared by Genetika. For the production of butanol, *Clostridium B-10939* strains in the flour