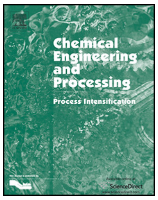
Chemical Engineering and Processing 104 (2016) 201–211

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep



Energy saving potential of hybrid membrane and distillation process in butanol purification: Experiments, modelling and simulation

Antonia Rom*, Angela Miltner, Walter Wukovits, Anton Friedl

Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria

ARTICLE INFO

Article history:
Received 25 November 2015
Received in revised form 14 March 2016
Accepted 17 March 2016
Available online 18 March 2016

Keywords:
Pervaporation
Membrane distillation
Concentrating butanol solution
User defined unit
Energy savings
Process simulation

ABSTRACT

Pervaporation experiments of dilute aqueous butanol solutions were carried out with three PDMS [poly (dimethyl siloxane)] membranes. Based on the experimental results of the best performing membrane a regression for both butanol and water permeability was done in the software R and implemented in a user defined pervaporation unit operation in the software Aspen Custom Modeler. With the implementation of the pervaporation step in Aspen Plus the hybrid pervaporation and distillation purification chain can be simulated in consistent way.

Calculation of pervaporation of a 0.5 wt% BuOH-water solution with the experimentally investigated PDMS membrane results in a permeate stream with a concentration of 9 wt% BuOH. Application of membrane distillation resulted in a permeate butanol concentration of only 3 wt% and a considerable higher specific energy demand compared to pervaporation.

For product purities of 99 wt% of BuOH a hybrid pervaporation and distillation process saves around 50% of the energy demand compared to state of the art distillation. A sensitivity analysis of the pervaporation step reveals, that for the hybrid pervaporation and distillation process compared to state of the art distillation the energy demand decreases already exceeding 5 wt% BuOH in the permeate stream.

1. Introduction

Biobutanol is one of the most promising but not yet implemented biofuels. Although it has advantages over ethanol in terms of higher heating value, low corrosion and low vapour pressure, industrial production is quite inefficient [1]. Biobutanol is mostly produced via Acetone-Butanol-Ethanol (ABE) fermentation, which is one of the oldest industrial processes. Prior to the 1950s, all butanol was produced via this process, but low product concentration due to product inhibition of microorganisms at 13 g/l BuOH, resulted in a non-competitive overall process [2]. At such low feed concentration, the downstream processing via distillation consumes enormous amounts of energy [3]. Therefore, online separation of butanol during continuous fermentation is desired to keep butanol concentration under the inhibition level and obtain high sugar conversions [4,5]. This can be achieved by integrating the fermentation with in situ product recovery such as gas-stripping, extraction, adsorption, membrane distillation and pervaporation [6,7]. Vane [8] and Qureshi et al. [7] reported, that the most energy efficient methods for recovery of organic compounds from fermentation broths are pervaporation and gas stripping. Pervaporation (PV) is a thermal driven membrane separation process and has advantages in terms of high selectivities compared to membrane distillation (MD), with its high transmembrane fluxes. Membrane separation processes for in-situ recovery are the focus of many researchers, but membrane fouling may occur, especially when a fermentation broth is present on the feed side [9]. As an alternative gas stripping is under investigation. Gas stripping can easily be implemented with any harm to the fermentation process and only volatile products are stripped from the broth. However, the vapour liquid equilibrium cannot be exceeded and the recovery of the products from the broth is again energy demanding, since low temperatures are necessary [10].

The focus in this paper is set on the membrane separation processes pervaporation and membrane distillation. Matsumura et al. [3] reported, that enormous amounts of energy can be saved, processing BuOH-water mixtures having BuOH concentrations of 10 wt% and higher. Vane [8] also demonstrates the possibility of energy savings possible with a single-pass pervaporation step for BuOH purities of 80 wt%. This is enabled by the highly non-ideal vapour liquid equilibrium of butanol-water mixtures. Butanol has a very high activity coefficient at low concentrations and the aqueous system shows a miscibility gap between 7.7 and 80 wt% BuOH [11,12]. The goal of in situ membrane separation processes (e.g. pervaporation

---

* Corresponding author.
E-mail address: antonia.rom@tuwien.ac.at (A. Rom).

http://dx.doi.org/10.1016/j.cep.2016.03.012
0255-2701/© 2016 Published by Elsevier B.V.

Nomenclature

A	Membrane area: [m^2]
c	Feed butanol concentration: [wt%]
J	Transmembrane mass flux: [$kg/m^2\,h$]
m	Mass: [kg]
M	Molar flux: [kmol/h]
N	Transmembrane molar flux: [$kmol/m^2\,h$]
p	Pressure: [bar]
p^{sat}	Saturation pressure: [bar]
P	Permeability: [kmol/m3hbar]
$\frac{P}{\delta}$	Permeance: [$kmol/m^2hbar$]
q	Specific energy requirement: [MJ/kg]
R	Ideal gas constant: [kJ/kmol K]
t	Time: [h]
T	Temperature: [C]
A, B, C, D, E	Regression coefficients: [-]
V	Volume flow: [l/h]
w	Weight fraction: [kg/kg]
W	Specific energy requirement: [kJ/mol]
x	Molar fraction in liquid phase: [kmol/kmol]
y	Molar fraction in vapour phase: [kmol/kmol]

Indices

feed, f	Feed side of the membrane
i, j	Component i, j
n	Number of cell
perm, p	Permeate side of the membrane
ret	Retentate side of the membrane
1, 2	Inlet and outlet stream of vacuum pump

Greek letters

α	Selectivity: [-]
β	Separation factor: [-]
δ	Thickness of the selective layer: [m]
γ	Activity coefficient: [-]
κ	Isentropic coefficient: [-]

or membrane distillation) is to raise butanol concentration into the two phase region to obtain the advantage of the intrinsic separation, as can be seen in Fig. 1. Obtaining very high purities are not possible in a single separation step up to now. The butanol rich phase can then be purified in an efficient distillation step.

Pervaporation is a thermal driven membrane separation process applying dense polymeric or ceramic membranes in contact with the liquid to selectively remove components. In pervaporation the membrane has a selective layer, which leads to high separation factors exceeding 100 for butanol-water mixtures or even higher values in other binary systems [13,14]. This, and the fact that in pervaporation only the permeate stream is evaporated, makes it more efficient compared to other phase changing processes, like standard distillation [15]. In pervaporation the driving force is the partial pressure difference between the feed and the permeate side. For dense polymeric membranes separation is further influenced by the affinity of the component to diffuse in the dense membrane, following the solution – diffusion model of Wijmans and Baker [16]. Applying microporous ceramic membranes the Knudsen diffusion model describes the transport in the pores. This mechanism becomes dominant, when the main free path of the gas molecules is much greater than the pore size of the membrane.

The Knudsen diffusion model also describes the transport through the porous membranes in membrane distillation, another membrane separation process which can be applied for the recovery of organic solvents from fermentation broth. In membrane distillation the hydrophobic porous membrane has no selective layer, but the pores provide the surface for the evaporation step [17]. Therefore vapour liquid equilibrium cannot be exceeded, but higher fluxes are possible compared to pervaporation with dense membranes [18]. Membrane distillation is already implemented in industry for water desalination. However, membrane wetting can occur during MD, which causes a flux decline and has to be taken into account for industrial application [19].

Besides dehydration as demonstrated by Chapman [20], main application of pervaporation is the separation of volatile organic compounds from aqueous or organic solutions [13]. Alcohol recovery in general, but especially butanol separation from fermentation processes has been extensively investigated in the literature [8,21–26]. In the work of Rozicka et al. [27] polymeric membranes were investigated in binary alcohol water solutions at a feed temperature of 25 °C. Further investigation was done by Kujawska et al. [28] where the focus was on various binary water solutions at 4 wt% and 30 °C feed temperature. Pervaporation experiments with PDMS membranes to separate ABE model solutions at 65 °C were reported in the work of Kujawski et al. [29]. Such high concentrations exceed the inhibition level, and do not reflect fermentation process parameters during ABE-fermentation. In ABE fermentation BuOH feed concentrations around 1 w% at a temperature of 35 °C is observed [1]. Therefore further investigation was needed to reflect the influence of concentration and temperature level on butanol recovery. Hence in this paper pervaporation experiments with PDMS membranes were performed at low BuOH concentration of 0.5–1.5 wt% and at feed temperatures of 25–55 °C to obtain process data relevant for in situ solvent recovery during ABE-fermentation.

Intention of this paper is to underline the energy saving potential of a hybrid membrane separation (pervaporation, membrane distillation)-distillation step in biobutanol separation compared to state of the art distillation. The possibility of separation close to the boiling point, as well as separating heat-sensitive and azeotropic mixtures makes pervaporation interesting

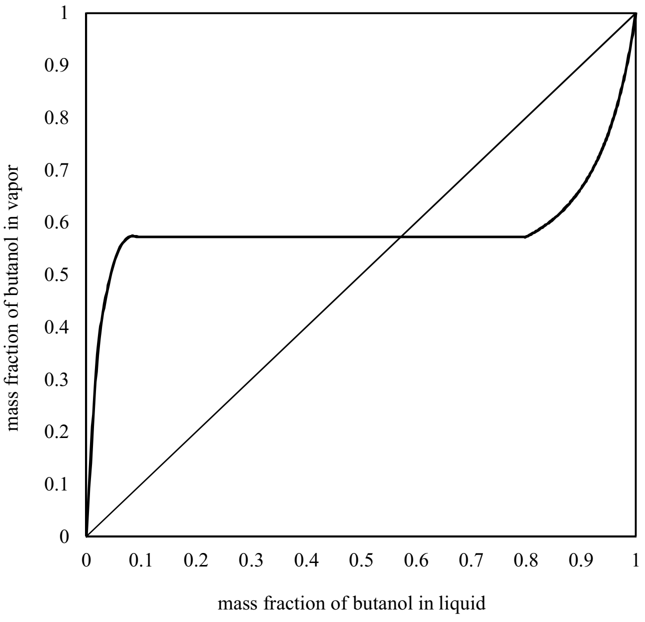


Fig. 1. Vapor-liquid equilibrium of butanol–water system, calculated in Aspen Properties with NRTL user properties from [12].