

# Technical Optimization of a Treatment Process on ABE Effluent by Membrane Technologies

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## Abstract

In the last decades, the interest in biofuel production is sensibly growing as a good source of sustainable energy and a valid alternative to fossil ones. One of the most promising biofuel is butanol and might be produced by starting from different substrates, such as second generation ones, that have the advantage to be in the future more cost effective, as soon as the relevant production processes will be fully developed and optimized.

In this case, the entering lignocellulosic material undergoes biological digestion up to a mixture mainly of acetone, butanol and ethanol, respectively. The digestion product, called ABE, requires the separation of almost pure butanol from the other components, in order to qualify as a biofuel. A possibility to perform this separation is by fractioned distillation, which has the advantage to be operated with ease, but leads to very high operating costs.

In this work, the separation of n-butanol from ABE was performed by means of membrane technology in four subsequent steps: ultrafiltration (UF), pervaporation (PV), nanofiltration (NF) and a last step of demixing once the n-butanol concentration reaches values within the miscibility gap. The study focused on the productivity, selectivity and longevity of the adopted membranes; in particular, it was observed by experimental campaign that membrane fouling must be strongly inhibited to achieve technical and economic feasibility of the overall proposed process.

**Keywords:** ABE wastewater, biofuel, butanol, membranes, fouling

## 1. Introduction

In the last years, butanol biofuel production from ABE is gaining again much interest (Karimi et al., 2015). The approach adopting membranes certainly has advantages compared to other conventional techniques, but there is a problem of fouling which significantly reduces its performance over time. Membrane fouling may be sensibly inhibited by fixing operating conditions below the boundary flux  $J_b$  (Stoller and Ochando-Pulido, 2014). Nevertheless, UF is not sufficient to reach n-butanol concentrations useful for the production of biofuels, therefore other post-treatment processes are required. The use of pervaporation to concentrate the streams from the ABE process have been studied in laboratory and

industrial level with excellent results (Van Wyk et al., 2017). In this work, pervaporation will be used on the UF permeate. After this, NF is employed to reach final butanol targets.

The membrane performances of an ultrafiltration (UF), pervaporation (PV) and nanofiltration (NF) in series for the recovery of n-butanol from ABE streams are here reported, with insight to avoid membrane fouling by sub-boundary operating conditions (Stoller and Ochando Pulido, 2014).

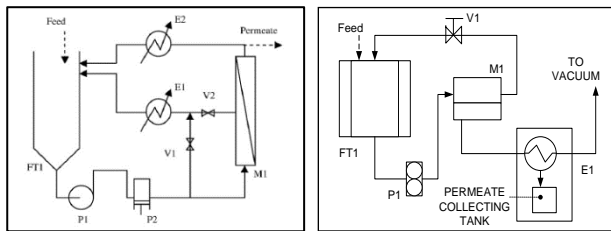
## 2. Methods

Two different lab scale membrane plants were used during this study.

UF and NF were performed using the plant reported in Figure 1 (left). It consists of a 100 liter feed tank, FT1, in which the pretreated feedstock is carried. The centrifugal booster pump, P1, and the volumetric pump, P2, drive the wastewater stream over the used spiral wounded ultrafiltration (UF model GM supplied by Osmonics) or nanofiltration (NF model DK supplied by Osmonics) membrane, fitted in the housing, M1, at an average flow rate equal to  $600 \text{ L h}^{-1}$ . The active membrane area of both the modules are equal to  $0.51 \text{ m}^2$ . The maximum allowable operating pressure is equal to 16 bar and 32 bar for UF and NF, respectively. The temperature was controlled for all experiments at the value of  $20 \pm 1^\circ\text{C}$ . After each experiment, the membrane was rinsed with tap water for at least 30 min.

For PV a smaller unit was adopted. Compared to the previous one, the PV lab scale plant uses flat sheet membranes type CMC-VP-31 supplied from Celfa (M1), with a surface area equal to  $44.2 \text{ cm}^2$ . The temperature is kept constant at a value of  $20 \pm 1^\circ\text{C}$  by the jacket of the feed tank vessel FT1. Only one valve (V1) is available to control the operating pressure on feed side. On the permeate side, a vacuum pump guarantees a constant pressure value equal to 0.05 bar. In order to capture all the permeate stream, a quenching device E1 is connected between the membrane and the pump, operating at  $-5^\circ\text{C}$ , enough to quickly condensate all the components in the permeate stream and collect them in a collecting vessel

within E1. The scheme of the adopted plant is shown in Figure 1 (right).



**Figure 1.** Scheme of the adopted experimental set-up

### 3. Results And Discussion

The characteristics of the raw ABE stream used in this study were reported in Table 1, first line.

Concerning UF, in a first step the boundary flux and  $\alpha$  values were determined. A value of  $J_b$ ,  $TMP_b$  and  $\alpha$  equal to  $14.9 \text{ l h}^{-1} \text{ m}^{-2}$ , 5 bar and  $33.3 \cdot 10^{-3} \text{ l h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$  were found, respectively. Once determined, the separation of the permeate stream was performed by using a  $TMP$  value equal to 80%  $TMP_b$ . The operation reached a recovery value  $Y$  equal to 70%. From Table 1 it is possible to observe that indeed UF do not reject ABE components (very low rejection values  $R$ ); on the other hand, this pre-treatment appears to be mandatory: all the suspended solids and biomasses (SS) in the ABE stream are completely retained (data not here reported), permitting ease of use of the next separation step.

The obtained UF permeate stream was then submitted to PV. In this case, the boundary flux value was measured by calculation of a  $TMP_b$  value: starting from one definition of the boundary flux, that is at infinite operating time, the permeate flux will decrease by a value equal to  $\alpha$  and  $J_p$  will assume values equal to  $J_b$  if the  $TMP$  value do not vary (Ochando Pulido and Stoller, 2014). Once determined, it is possible to estimate the value of  $J_b(0)$ , at the start of the experiment, by interpolation. A value of  $J_b$  and  $TMP_b$  of  $2.9 \text{ l h}^{-2} \text{ m}^{-2}$  and 1.99 bar were calculated, respectively.

From table 1, it might be observed that the hydrophilic pervaporation membrane used in this experiment is very permeable to water, but not to organics. Therefore, n-butanol is concentrated in the concentrate and indeed the PV concentrate was used as feedstock to NF.

Again, for NF, the boundary flux and  $\alpha$  values were determined. The results were reported in Figure 4. A value of  $J_b$ ,  $TMP_b$  and  $\alpha$  equal to  $23.5 \text{ l h}^{-1} \text{ m}^{-2}$ , 5 bar and  $66.7 \cdot 10^{-3} \text{ l h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$  were found, respectively. Once determined, the separation of the permeate stream was performed by using a  $TMP$  value equal to 80%  $TMP_b$ . The operation reached a recovery value  $Y$  equal to approx. 70%.

Table 1 reports the characteristics of all streams. The target stream is the NF concentrate. Demixing of the NF concentrate is in ratio 1:10, at 72% in n-butanol.

### 4. Conclusions

It is possible to see that the suggested process is technically feasible, but do not reach the desired final concentration of n-butanol in the NF permeate stream. Nevertheless, a final distillation step appears to be mandatory for post-processing the resulting NF concentrate to reach the desired specifications in n-butanol and to separate from ethanol. On the other hand, this last distillation step is performed on a smaller volume (0.8% of the initial one) and more concentrated (28 times initial n-butanol), leading to a less intensive and less costly operation.

As a future work, economic evaluation will be performed to compare the savings in using membrane technologies as a pre-processing step to distillation for ABE streams, in particular on the use of PV. Moreover, the use of reverse osmosis may be considered to achieve optimized starting concentrations to the final distillation column.

**Table 1.** Characteristics of all the streams

Stream	Water		Butanol		Ethanol		Acetone		SS	
	Conc	R	Conc	R	Conc	R	Conc	R	Conc	R
<b>Raw</b>	90.28% wt	-	0.54% wt	-	0.04% wt	-	0.14% wt	-	9.00% wt	-
<b>UF perm</b>	99.34% wt	0.09	0.49% wt	0.00	0.04% wt	0.00	0.13% wt	0.07	0.00% wt	1.00
<b>PV conc</b>	97.78% wt	0.93	1.62% wt	0.98	0.39% wt	0.98	0.11% wt	0.90	0.00% wt	-
<b>NF conc</b>	80.54% wt	0.95	15.31% wt	0.66	3.24% wt	0.66	0.91% wt	0.83	0.00% wt	-

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