Organophilic Pervaporation of Butanol from an Aqueous Solution with POMS

Antonia Rom*[,a], Diana. Esteve[b], Anton Friedl[a]

[a]Institute of Chemical Engineering, Vienna University of Technology, Getreidemarkt 9/166, 1060 Vienna, Austria
[b]School of Industrial Engineering, Polytechnic University of Valencia, Camino de Vera s/n, 46022 Valencia, Spain
antonia.rom@tuwien.ac.at

Butanol is seen as a promising biofuel due to its good fuel properties. In the biotechnological production of butanol by using Aceton-Butanol-Ethanol (ABE) Fermentation, the product inhibition of microorganisms at 13 g/L is a major problem. Due to the low butanol concentration present in the broth, state of the art distillation results in a highly uneconomically energy demand. To counteract this inhibition an on-line butanol separation is desirable. A two-step separation process with downstream distillation leads to a low overall energy demand and an optimized efficiency. An attractive option to put this into practice is the product separation with organophilic pervaporation.

This study focuses on the separation performance of a poly(octhylmethyl siloxane) [POMS] membrane during pervaporative stripping of butanol from an aqueous solution. The influencing factors on the pervaporative separation like feed temperature, alcohol concentration, Reynolds number in the module as well as the set vacuum were investigated in order to find optimum process conditions. Feed temperature varied from 25 to 55 °C, initial feed concentration from 0.5 to 1.5 w% and volume flow from 100 - 200 L/h. The applied vacuum was set to the lowest possible value and varied from 10 - 4 mbar depending on the flux influenced by process parameters. On account of numerous investigated parameters a model was generated with design of experiment, which should summarize all interesting process conditions. The experimental results show that POMS membrane can selectively separate butanol from an aqueous solution. The highest selectivity was obtained at temperature of 55 °C and low feed concentration of 0.5 w%. The applied vacuum at this process conditions stayed at about 10 mbar. Selectivities of about 28 are reached.

A prior work analysed POMS membranes during pervaporative stripping of ethanol from aqueous solutions. Experiments with similar process conditions were investigated to compare the data obtained in this study with others given in the literature. The trend of increasing selectivity at low alcohol concentrations and high temperatures is concordant during all experiments for ethanol as well as for butanol. This conformity assures the aim of this study showing pervaporation as a great possibility to raise the efficiency of the overall process and to deal with the low butanol concentration obtained during ABE-Fermentation.

1. Introduction

Biofuels are receiving much more attention in the last years, even though biofuels are no novel invention concerning the first Otto combustion engines running with ethanol. Also the quotation of Henry Ford 1925: "The fuel of the future is going to come from fruit like that sumac (shrubby tree) out by the road or from apples, weeds or sawdust, almost anything. There is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years." should forecast a wide use of biofuels almost one hundred years later (Kotrba, 2007).

Still the world's energy system is largely based on fossil fuels, but there is a new upcoming star in the battle of fuels: bio based butanol. Butanol with its higher energy content, lower water absorption, better blending ability and the possible use in engines without modification assure enormous potential. Despite

all these advantages compared to ethanol butanol has still too many drawbacks, which results in a highly uneconomical process (Dürre, 2007).

Product inhibition at about 13 g/L (Garcia et al., 2011) causes a dilute final product, which yields in an expensive down streaming process. Metabolic engineers focus on new strains with a much higher inhibition level (Xue et al., 2012). Further high research focus is centered on product recoveries, because state of the art distillation is not cost effective. An on-line butanol separation prevents inhibition level and a high sugar conversion rate is possible. Investigated recovery processes are gas stripping, liquid-liquid extraction, adsorption, membrane distillation and pervaporation (Vane, 2008).

Pervaporation with its simplicity, energy savings as well as nontoxicity to fermentation organism is considered to have the greatest potential (Qureshi et al., 1992). Commercially available membranes such as PDMS (polydimethylsiloxane) have been investigated in several works, resulting in separation factors of 16.7 and a high sugar conversion (Liu et al., 2011).

Lazarova (2012) analyzed the PV-application with POMS membrane for ethanol separation obtaining better results compared to reported literature with PDMS membrane. The aim of this work was to investigate the POMS membrane for the use of butanol recovery from aqueous solutions.

One reason why PV is a promising separation process for butanol-water mixtures lies in the highly non-ideal vapor-liquid equilibrium of this mixture. At very low concentrations as provided in the fermentation broth butanol has a very high activity coefficient.
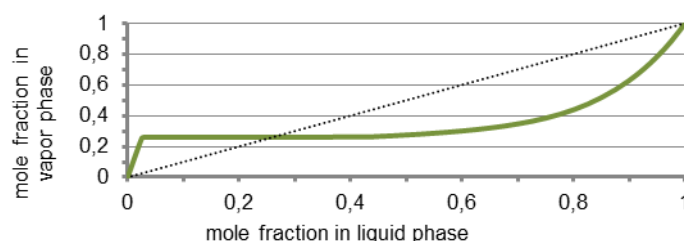

Figure 1: Vapour-liquid Equilibrium of 1-butanol/water mixture at atmospheric pressure (Gmehling et al., 1981)

Driving force of the PV process is the partial pressure difference between liquid feed and vapor permeate multiplied with Pi as the permeance, which characterizes membrane properties.

$$J_i = P_i \left(x_i p_i^{sat} \gamma_i - y_i p_{perm} \right)$$

(1)

The butanol activity coefficient of about 54 at 35 °C and a concentration of 5 g/l yields in a high separation factor, which at its best induces a two phase permeate. Additionally the use of high selective organophilic membranes leads to even higher recoveries. During this work the influence of feed temperature, flow rate, feed concentration and vacuum pressure on selectivity and butanol flux was explored during application of a POMS membrane in a PV apparatus.

2. Materials and Methods

2.1 Material

The membranes used were supplied by GKSS, Germany. Both membranes consist of the same material, a poly(octhylmethyl siloxane) skin layer on a poly(acrylonitrile) support. A difference between the two membranes is the production year. The first membrane, which is further called "old POMS", was produced some years earlier than the second membrane. The second membrane was ordered in the year 2012. Butanol 100 % was acquired from Merck, Germany, to prepare a butanol-water model solution with alcohol concentrations varying from 0.5 to 1.5 w%. Liquid nitrogen was acquired from Air Liquide, Austria.

2.2 Pervaporation

All the experiments were performed on a lab scale pervaporation setup. The setup is shown in Figure 2. The feed cycle contains a liquid reservoir on a balance, a gear pump, which circulates the feed at flow rates between 100-200 L/h, a heat exchanger and a flat sheet module with an active membrane area of 144 cm². Temperature was varied between 25 to 55 °C.

The membrane module consists of a stainless steel corpus with a Teflon inner surface. The permeate pressure was obtained by an oil sealed rotary vane vacuum pump from Oerlikon Leybold, Germany, and

varied between 4-10 mbar. The permeate vapour was condensed in a cooling trap by a dewar filled with liquid nitrogen. The permeate was collected after each experiment to calculate separation factor and the transmembrane alcohol flux. Alcohol concentration in the feed was measured on a DE45 Delta Range density meter from Mettler Toledo, Austria. The process yields in permeate concentrations higher than 7.7 w% and therefore a two phase mixture with a constant concentration was achieved in the permeate.
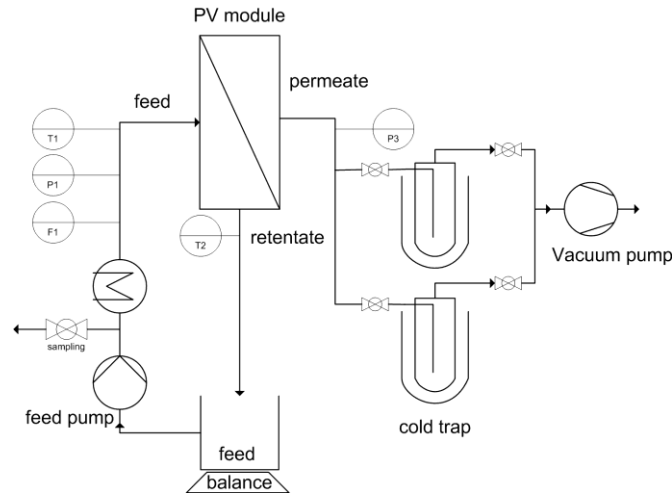

Figure 2: Flow sheet of pervaporation set up

The permeate flux is defined as

$$J_i = \frac{m_i}{At}$$

(2)

where J_i is the transmembrane component flux [g/m²h], m_i the mass of the component in the permeate [g], A the membrane area [m²] and t the experimental time [h].
The separation factor was calculated by mean of Eq (3):

$$\alpha_{ij} = \frac{w_{pi}\, w_{fj}}{w_{fi} w_{pj}}$$

(3)

where $w_{f,l}$ is the weight fraction in the feed and $w_{p,l}$ the weight fraction in the permeate.
After 1.5h duration time variation of feed concentration was negligible, due to a big enough feed volume.

2.3 Design of experiment (DoE)
On the basis of the huge amount of process variation a design of experiment was implemented with the help of the software statgraphics (Statpoint Technologies, Inc).

Table 1: DoE plan, which was used for pervaporation experiments with both membranes. Designed in Statgraphics.

Exp.	Temp. (°C)	Pres. (mbar)	%but	Flow (L/h)	Exp.	Temp. (°C)	Pres. (mbar)	%but	Flow (L/h)
1	55	4	0.5	200	11	55	10	1.5	200
2	35	7	1	150	12	25	10	1.5	100
3	25	10	0.5	200	13	55	10	1.5	100
4	55	10	0.5	200	14	35	7	1	150
5	25	4	1.5	200	15	55	10	0.5	100
6	25	10	1.5	200	16	55	4	0.5	100
7	25	4	1.5	100	17	35	7	1	150
8	35	7	1	150	18	55	4	1.5	100
9	25	4	0.5	200	19	25	4	0.5	100
10	55	4	1.5	200	20	25	10	0.5	100

Usage of the model decreases the numbers of experiments down to 20 runs. In this work a model 2^k was used, where k is the number of initial factors, like pressure and temperature. Every maximum and minimum of each initial factor is tested as well as four centre points to improve the reliability of the model. In Table 1 the experimental trial of the DoE model is listed. This trial was executed with both membranes to have comparable results.

3. Results and Discussion

In Table 2 all results of the experimental trials are listed. Discussion of the results was also done with help of statgraphics, which offers the possibility to plot e.g. temperature influence of all experiments in one diagram. In the first step a Pareto diagram was drawn, to see the most significant influence factors on butanol flux and selectivity. In this type of diagram the bright coloured column (+) represents high values and the dark column (-) low values (e.g. Figure. 3). The influence is plotted over the standard effect, which gives a hint for the quantity of the influence. In the second step the results were used to predict further experiments. Output of this investigation is an estimated response surface (e.g. Figure 4). In these graphics, each colour represents an interval of the response variable. At operating parameters of 55 °C and 1.5 w% highest flux and selectivity were obtained with both membranes. At this process conditions the membranes reached a total flux of 0.63 – 0.84 kg/m²h and a selectivity in the range of 41.2 – 42.9, being the new POMS with the higher values.

Table 2: Results of the old and the new POMS membrane

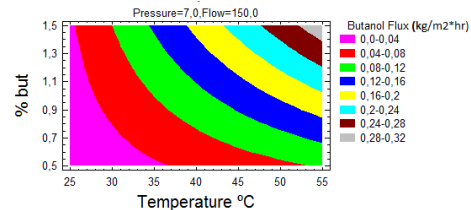|	Old POMS			New POMS		
	Vacuum pressure [mbar]	Total flux [kg/m²h]	Separation factor [-]	Vacuum pressure [mbar]	Total flux [kg/m²h]	Separation factor [-]
1	12	0.44676	39.19	15.33	0.56759	39.15
2	15	0.20000	20.03	19	0.26019	22.85
3	18.33	0.13194	17.28	22.16	0.15972	28.33
4	13.33	0.42176	35.17	16.16	0.53843	37.34
5	15	0.17500	21.28	20.16	0.21806	25.33
6	17.16	0.15463	17.75	20.33	0.20370	8.54
7	15.33	0.16204	18.74	21.16	0.17731	18.63
8	14	0.21111	23.99	17.66	0.27824	30.36
9	17.16	0.11852	15.62	21	0.15509	25.30
10	12.5	0.62917	40.90	17.16	0.86852	34.65
11	14	0.63704	41.20	15.33	0.84491	42.94
12	18.16	0.13380	12.15	20.5	0.17639	21.48
13	13.33	0.58194	36.18	15.16	0.78704	37.86
14	16.33	0.31944	16.28	18	0.26620	27.60
15	13.66	0.41296	26.12	15.5	0.54907	36.51
16	13.16	0.43426	23.90	15.66	0.53704	37.37
17	16.5	0.17546	22.90	18.66	0.26574	30.80
18	12.83	0.63843	39.40	15.33	0.80278	38.45
19	18.66	0.10278	18.29	19.33	0.15556	23.38
20	18.66	0.09074	20.24	20.33	0.14722	19.02

3.1 Influence on Butanol flux

Both membranes show the same response regarding the influences on butanol flux (Figure 3). The main factors are high temperature, high concentration and the interaction between both of them. This corresponds with the theoretical model of the driving force. With increasing temperature and concentration in the feed the partial pressure in the feed rises and yields in a higher flux. The standard effect of the new membrane up to 15 indicates high fluxes during the experiments.

-3a-

-3b-
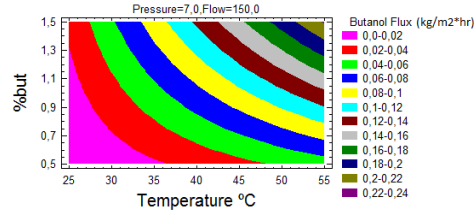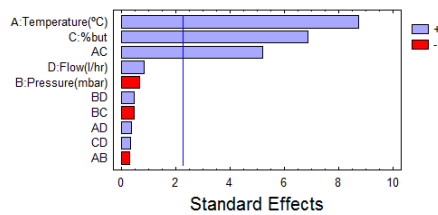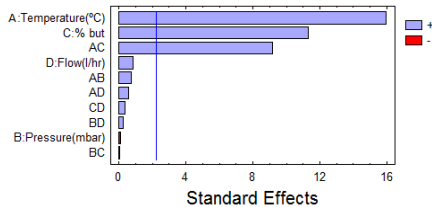
*Figure :. Pareto diagram for Butanol Flux, (a) old POMS (b) new POMS*

-4a-

-4b-

Figure :. Estimated response surface for Butanol Flux, (a) old POMS, R²= 0.94 and (b) new POMS, R²= 0.98, for p=7 mbar and flow 150 L/h
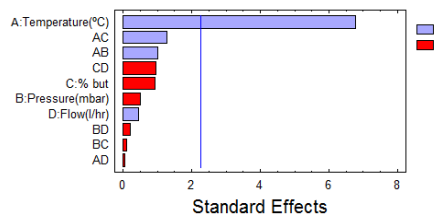
In Figure 4 the estimated response surface is plotted. Both membranes operate better at high temperatures and high concentrations. This conclusion confirms that the main influence factors for butanol flux are high temperature and high concentration. The new POMS membrane nevertheless has a better performance, resulting in a butanol flux of 0.28 -0.22 kg/m²h at a feed temperature of 55 °C and a feed concentration of 1.5 w%.
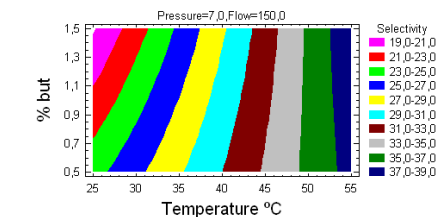
3.2 Influence on selectivity

Finally, the influence of process parameters on selectivity has been studied with the same method
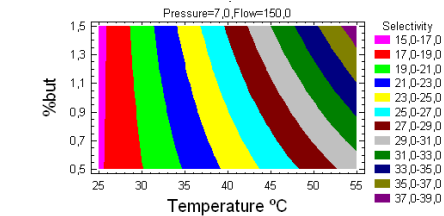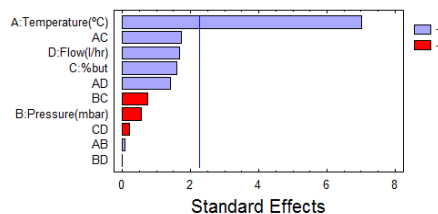
-5a-

-5b-

Figure 5: Pareto diagram for Selectivity (a) old POMS and (b) new POMS

-6a-

-6b-

Figure 6: Estimated response surface for Selectivity (a) old POMS, R²= 0.87, and (b) new POMS, R²= 0.85 for p=7 mbar and flow 150 L/h

The results show, that high feed temperatures result in high selectivity. The standard effect of both membranes in Figure 5a and b is similar, due to similar results obtained during the experiments (Table 2). Interesting is the influence of the feed concentration; however it is not statistically significant. Different to the old membrane the new one shows a better performance at low alcohol concentrations (Figure 6). At 35 °C and 0.5 w% the old POMS has a selectivity of 21, but the new POMS nearly 29. At low temperatures the new POMS is more influenced by feed concentration, performing better at 0.5 w%.

4. Conclusions

The results of this work show good correlation with obtained data of Lazarova (2012). In her work high temperature and high concentration increase alcohol flux and selectivity. The investigation of the old POMS membrane, which was the same batch Lazarova used, showed different results. Instead selectivity decreased with higher feed concentration the selectivity increased. One conclusion might be a kind of surface change due to the long storage. This could affect the performance of the POMS membrane resulting in different response surfaces. Investigation of the new POMS membrane agrees in principle. At estimated 35 °C and low concentrations the new POMS membrane operates at selectivities of 29. Increasing temperature yields in higher fluxes and selectivities. Obtained data proved the aim of this work, that POMS is a suitable membrane for the application during the ABE-Fermentation dealing with very low concentrations.

Future work focuses on the investigation of other organophilic membranes with the 2^k model as well as an application of the PV-apparatus during a continuous ABE-fermentation.

References

Dürre P., 2007, Biobutanol: An attractive biofuel, Biotechnology Journal, 2, 1525-1534

García V., Päkkilä J., Ojamo H., Muurinen E., Keiski R.L.,2011, Challenges in biobutanol production: How to improve the efficiency?, Renewable and Sustainable Energy Reviews, 15, 964-980

Gmehling J., Onken U., Arlt W., 1981, Vapour-Liquid Equilibrium Data Collection 1a, Chemistry Data Series, 1, 329

Kotrba R., 2007, Ethanol Producer Magazine <www.ethanolproducer.com/articles/2863/moments-of-reflection/> accessed 24.05.2013

Lazarova M., Bösch P., Friedl A., 2012, POMS Membrane for Selective Separation of Ethanol from Dilute Alcohol-Aqueous Solutions by Pervaporation, Separation Science and Technology, 47, 1709-1714

Mariano A.P., Costa C.B.B., De Angelis D., Maugeri Filho F., Atala D.I.P., Wolf Maciel M.R., Maciel Filho R.,2010, Dynamics of a continuous flash fermentation for butanol production, Chemical Engineering Transaction, DOI: 10.3303/CET1020048

Qureshi N., Maddox I.S., Friedl A., 1992, Application of Continuous Substrate Feeding to the ABE Fermentation: Relief of Product Inhibition Using Extraction, Perstraction, Stripping, and Pervaporation, Biotechnology Progress, 8, 382-390

Vane L., 2008, Separation technologies for the recovery and dehydration of alcohols from fermentation broth, Biofuels, Bioproducts and Biorefining, 2, 553–588

Xue C., Zhao J., Lu C., Yang S.-T., Bai F., Tang I.-C., 2012, High-titer n-butanol production by clostridium acetobutylicum JB200 in fed-batch fermentation with intermittent gas stripping, Biotechnology and Bioengineering, 109, 2746–2756