Separation Techniques for Distillery Stillage Treatment

Kateřina LAPIŠOVÁ, Roman VLČEK, Jana KLOZOVÁ, Mojmír RYCHTERA and Karel MELZOCH

Department of Fermentation Chemistry and Bioengineering, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic

Abstract

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The separation of stillage was tested by means of the pilot plant ARNO 600-BIO using three-channel ceramic membranes with the pore diameter range from microfiltration to ultrafiltration (1.4 μm–5 kDa). The permeate from the last membrane step was able to be recycled as technological water. The best results were achieved in the arrangement of series using 0.2 μm membrane as the first step supplemented by ultra-filtration membranes (50 kDa and 15 kDa), predominantly, where the reduction of the chemical oxygen demand (COD) extended 80%. With this process, we try to get some advantages over the conventional process in terms of eliminating both land and energy costs for the wastewater treatment process and improving the quality of the discharge water. The main goal in this study is to analyse different separation steps and conditions to find both the best separation options for the decrease of the final volume of distillery stillage, and the way how to make the bio ethanol production more profitable.

Keywords: distillery stillage; bio ethanol; membrane filtration; ceramic membranes

There exists a great possibility to produce bio ethanol from agricultural crops grown in marginal areas of the Czech Republic, where the production of cereals in the food grade quality is not profitable. With the enlargement of the bio ethanol (fuel ethanol) production, the increasing amounts of secondary products, esp. distillery stillage, becomes a hardly solvable problem which requires an ffective stillage management (Sheehan & Greenfield 1980; Chotěborská *et al.* 2004).

A new clean technology was applied in the ethanol production industry to eliminate the end of the pipe technology currently used for the treatment of the distillery waste. Membrane technologies offer one possibility to improve further the quality of the waste water (Kentish & Stevens 2001).

Distillery stillage is made up of the solid and liquid effluents remaining after ethanol distillation at the bottom of the distillation column. The amount and quality of stillage are highly variable and dependent on the feedstocks and various aspects of the ethanol production process. It has high concentrations of organics, chemical oxygen demand (COD) up to 100 g O_2/l, and total solids (8% wt), low pH values (3), and a very large volume increasing together with the ethanol production. The ratio between the amount of ethanol and the stillage production is highly disproportional. To produce 1 l of

ethanol, however, approximately 10 to 15 liters of distillery slops are generated. The size and the shape of particles are very variable and depend on the pretreatment of the cereals at the beginning of the distillery process (Wilkie *et al*. 2000).

Stillage is not further utilised very economically (usually as a fertiliser or cattle feed) although it can be used as a raw material for other fermentations to provide a carbon source and other fermentation media components. Besides starch, dextrin, and other sugars already converted to ethanol, stillage contains all other non-volatile substances of the raw material used, in more or less converted conditions: lipids and protein degradation products thereof, vitamins, minerals and fibrous material. In addition, stillage contains all yeasts grown during fermentation. This content of the considerable amount of yeasts affects the increase of the economic value of the stillage by a surplus of proteins, amino acids, vitamins, and further growth supporting compounds (Maiorella *et al.* 1983; Hinková *et al.* 1998).

Stillage, once generated, is usually treated first with a screw decanter to remove solids, followed successively by anaerobic digestion and activated sludge treatment. Even with such a complicated treatment system, it is quite difficult and sometimes impossible to meet the effluent discharge limit. Although the biological treatment process has several advantages such as an easy access and a large scale operation, the major drawbacks of the process are its high energy consumption (30% of the total energy), high labour costs, and large variations of the treatment efficiency with the change in raw materials used for the ethanol fermentation. Separation technologies make it possible to eliminate the stillage treatment step using the conventional biological waste treatment processes such as anaerobic digestion and activated sludge step currently used in industry (Kim *et al.* 1997).

The ceramic membranes may be the ideal solution as they are highly selective, resistant to high temperatures and solvents and very stable, having a long life span. The wasted energy in this process is lower than in other procedures such as evaporation. Nevertheless, there are some limitations to the use of these membranes; modest fluxes, a high investment necessary to obtain a ceramic membrane unit, and the fouling (the blockage of the pores), which can be considered the main concern of this technique (Sondhi *et al.* 2003; Bruggen *et al.* 2004).

MATERIAL AND METHODS

Raw materials. The biggest benefit of this project resided in the real separation material application in the pilot plant. For the realisation of this project, the potato stillage from the distillery Liho-Blanice (CR) was used.

Before each separation series, the stillage was decanted in order to remove coarse particles and thus to improve the efficiency of the process, not only by the removal of pollutants, especially solids, but also by diminishing the fouling effect. Therefore, only the thin stillage was used to perform the separation. In order to prevent contamination, the stillage, as well as all the samples, were frozen.

Separation unit. All the experiments were conducted in the pilot unit Arno 600-BIO (Mikropur Ltd., Hradec Kralové, CR). This unit was used as a typical separation unit for: micro-filtration, ultra-filtration, and nano-filtration, with the pumping capacity of 600 l/h and maximal operating pressure of 6 MPa.

The unit was fitted just with one membrane module, so the trials were realised in batch mode. When the first separation step was finished, the permeate was stored for the next step and the membrane used was cleaned in the module or in the bath. Then the membranes were changed and the trial continued with the permeate from the first step, so the volume of inlet was reduced as compared with the first step.

Ceramic membranes. Several separations performed to treat the stillage were conducted in cross flow three-channel ceramic membranes prepared by sintering the mixture of Al_2O_3, TiO_2 and ZrO_2 (TAMI Deutschland) (Table 1).

Analytical methods. Several parameters were determined in both the permeate and the concentrate samples: chemical oxygen demand (COD); total solids; reducing compounds; total nitrogen (Malý & Malá 1996), to evaluate the influence of each separation step.

– COD – determined spectrophotometrically at 600 nm after oxidation with $K_2Cr_2O_7$;
– total solids – dried in a stove at the temperature of 105°C until achieving the constant weight;
– reducing compounds – determined by the Schoorls method;
– total nitrogen – determined by the Kjeldahl method.

Separation process. The membrane separation characteristics were studied together with the

Table 1. Membrane characteristics, operational parameters

Material	Al_2O_3, TiO_2, ZrO_2
Length	550 mm
Membrane diameter	10 mm
Channel diameter	3 mm
Number of channels	3
Filtration surface area	0.021 m^2
Crossflow velocity	7.86 m/s
Transmembrane pressure	10 kPa
Process temperature	30°C
Mechanical resistance	9 MPa
Chemical stability	0–12 pH
Maximum temperature	350°C
Steam sterilisation	121°C
Membrane pore size	Water flux (l/hm^2MPa)
0.2 μm	14 290
300 kDa	7 430
150 kDa	3 710
50 kDa	2 860
15 kDa	1 370
8 kDa	1 200
5 kDa	710

cleaning mechanism. The process was evaluated from the point of view of the mass balance and the dynamics (total separation time, the decline of the filtration efficiency in the ceramic membranes-permeate flux, fouling effect, etc.).

The separation process was carried out in five, three, and finally two step membrane arrangements. The five and three step membrane arrangements were done to experience and confirm the course of the separation process (operational time, membrane regeneration). The aim of the further membrane steps reduction was operational cost savings with maintaining the same separation efficiency. The two step membrane arrangements met this, so they were realised predominantly, therefore just these results are published. Nine two step membrane trials dealing with potatoe stillage are presented.

Firstly, stillage was decanted to remove coarse solids and than it was usually treated by micro-

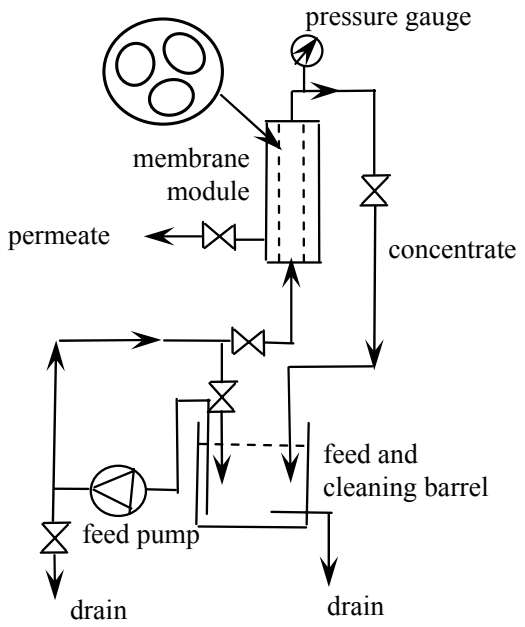

Figure 1. Schematic diagram of the pilot plant

filtration. The process temperature was maintained at a constant value of 30°C.

During the filtration, the concentrate was recirculated back to the feed tank and the permeate was collected in a separate barrel (Figure 1). Permeates from micro-filtration were further used as an inlet for ultra-filtration. Ultra-filtration of distillery stillage was carried out to remove all the suspended solids and other solid particles.

Membrane regeneration. The main concern of this technique is the fouling, where especially the membranes with a smaller pore size (ultra-filtration, nano-filtration) were very sensitive to this effect (Lim & Bai 2003).

Several cleaning methods were tested. Regeneration of the membranes was performed inside the membrane module using a recirculation solution of commercial detergents (Divomyl and Divos 124 from Diversey Lever), sodium hydroxide and hydrogen peroxide in various concentrations used separately or by turns or outside the module submersing the membrane into the cleaning solution. The possibility to heat the membrane in an eletric oven at 560°C was also tested.

RESULTS AND DISCUSSION

Distillery stillage treatment

The separation series realised with two step membrane arrangements are summarised in Table 2. The process parameters (stillage mass, filtration dura-

Table 2. Experiments with two step membrane arrangements

Series	Membrane pore size						
	0.2 µm	300 kDa	150 kDa	50 kDa	15 kDa	8 kDa	5 kDa
I	+	+					
II	+		+				
III	+			+			
IV	+				+		
V		+		+			
VI			+	+			
VII			+		+		
VIII				+		+	
IX					+		+

tion, flux reduction) are summarised in Table 3. The analytical results, decreasing amounts of stillage components at the end of the separation process (permeate output), using 0.2 µm membrane as the first step, as compared with thin stillage (inlet), are showed in Table 4. Table 5 summarises the removal efficiency of the analytes in percentage at the end of the separation process.

Table 3. Summary table of the process parameters

Separation series/ membrane		Stillage mass (g)		Filtration duration (min)	Flux (l/hm^{2}MPa)	
		inlet	outlet*		inlet	outlet
I	0.2 µm	5040	3385**	90	2715	400
	300 kDa		2240	80	1140	685
II	0.2 µm	4795	3160	80	1770	915
	150 kDa		2030	95	1200	460
III	0.2 µm	6080	4290	20	3300	1390
	50 kDa		2320	35	860	640
IV	0.2 µm	4850	3150	40	2780	1110
	15 kDa		1890	100	650	220
V	300 kDa	4900	3280	80	1110	390
	50 kDa		1800	80	1220	280
VI	150 kDa	5025	3470	105	1110	780
	50 kDa		1760	80	1555	420
VII	150 kDa	5150	3605	75	970	500
	15 kDa		2090	105	580	167
VIII	50 kDa	4980	3140	75	890	330
	8 kDa		1980	100	460	440
IX	15 kDa	4850	3300	180	390	360
	5 kDa		1910	135	330	320

*permeate mass (g); **outlet of the first step = inlet to the second one

Table 4. A analytical results of potato stillage components at the end of separation process using 0.2 μm membrane as a first step

Analytical quantity	Separation series of potato stillage										
	I (0.2 μm; 300 kDa)			II (0.2 μm; 150 kDa)			III–IV inlet	III (0.2 μm; 50 kDa)		IV (0.2 μm; 15 kDa)	
	inlet[1]	inter.[2]	outlet[3]	inlet	inter.	outlet		inter.	outlet	inter.	outlet
Solids (g/kg)	22.7	17.7	11.9	24.2	18.9	13.7	19.8	15.4	8.1	13.9	9.3
COD (g O_2 /l)	44.0	31.5	29.5	40.4	37.4	25.6	93.7	85.3	22.5	66.5	26.2
Reducing component (g/kg)	2.0	1.5	1.2	1.8	1.3	1.0	1.0	0.5	0.3	0.7	0.5
Nitrogen (g/kg)	0.5	0.4	0.4	0.6	0.5	0.5	0.5	0.4	0.3	0.3	0.2

[1]thin stillage; [2]intermediate composition (0.2 μm); [3]final permeate from the second separation step (300 kDa)

Table 5. Removal efficiency for separation series using 0.2 μm membrane as the first step compared with initial thin stillage (each initial concentration is equal to 100%)

Removal efficiency	Separation series of potato stillage							
	I		II		III		IV	
	0.2 μm	300 kDa	0.2 μm	150 kDa	0.2 μm	50 kDa	0.2 μm	15 kDa
Solids (%)	22	47	22	43	26	59	30	53
COD (%)	30	33	8	37	9	76	29	72
Reducing component (%)	21	37	28	44	50	73	29	49
Nitrogen (%)	14	21	13	16	22	50	31	51

The object of the work was to obtain a cleanest permeate to reuse it as a technological water in fermentation processes. The results of the concentrate flow are not presented because the aim was to concentrate it maximally for the further use as an animal feed. The retentate fraction represented in both separation steps around 10 to 30% of the inlet volume of thin stillage and was concentrated approximately twice considering the inlet of thin stillage.

The stillage came from the same producer but in part at different periods, so the character of the separation material varied, which influenced the process and caused, probably, the differences and unpredictability of the experiment, but on the other hand presented a big contribution due to using a real material directly from the industry.

An important point of view for the evaluation of the whole separation efficiency is not only the amount of analytes but also the inlet stillage volume, flux decline, and the operational time.

The interpretation of the first experimental part applying micro-filtration membrane as the first step is that series III using 0.2 μm membrane supplemented by the 50 kDa membrane was evaluated as the best for the potato stillage treatment. The amount of analytes was reduced effectively, the removal efficiency was more than 50% for all the analytes determined, and the separation ran faster in comparison to other series (55 min) even at a higher inlet volume of stillage.

Table 6 presents the analytical results, the decreasing amount of the stillage components at the end of the separation process (permeate outlet), using ultra-filtration membranes as the first step, as compared with thin stillage (inlet). The percentage removal efficiency of analytes at the end of the separation process is summarised Table 7.

The separation series VIII and IX using nano-filtration membranes were very effective in the analytes removal, at around 80%, but the separation process ran at a higher pressure (up to 3 MPa) and filtration duration. The gradual increase of the pressure resulted in a constant permeate flux.

According to the analytical results and separation conditions, the series VII was the most effective

Table 6. The analytical results of potato stillage components at the end of separation process using ultra-filtration and nano-filtration membrane as the first step

Analytical quantity	Separation series of potato stillage										
	V–IX inlet	V 300 kDa; 50 kDa		VI 150 kDa; 50 kDa		VII 150 kDa; 15 kDa		VIII 50 kDa; 8 kDa		IX 15 kDa; 5 kDa	
		inter.	outlet	inter.	outlet	inter.	outlet	inter.	outlet	inter.	outlet
Solids (g/kg)	19.8	15.2	10.3	15.2	10.7	17.0	8.3	9.3	5.7	6.3	4.2
COD (g O_2 /l)	93.7	61.8	42.2	72.1	58.1	49.7	18.7	60.9	19.7	47.8	16.9
Reducing component (g/kg)	1.0	0.9	0.6	0.8	0.7	0.5	0.2	0.6	0.4	0.5	0.4
Nitrogen (g/kg)	0.5	0.2	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1

Table 7. Removal efficiency for separation series using ultra-filtration and nano-filtration membrane as the first step compared with initial thin stillage (each initial concentration is equal to 100%)

Removal efficiency	Separation series of potato stillage									
	V		VI		VII		VIII		IX	
	300 kDa	50 kDa	150 kDa	50 kDa	150 kDa	15 kDa	50 kDa	8 kDa	15 kDa	5 kDa
Solids (%)	23	48	23	46	14	58	53	71	68	79
COD (%)	34	55	23	38	47	80	35	79	49	82
Reducing component (%)	15	42	17	32	46	80	42	59	52	62
Nitrogen (%)	55	77	60	74	62	71	50	77	58	73

in potato stillage treatment using ultra-filtration membranes, 150 kDa membrane as the first step and 15 kDa membrane as the second one.

It is difficult to evaluate the separation experiments generally. The course of the process was not easy to predict. Even using the membranes with the smallest pore sizes from the nano-filtration area, the reduction of analytes was not always the highest as can be supposed and the process has to be realised at higher pressure.

Ceramic membrane regeneration

To check the fouling effect, the permeate flux was measured before, after, and during the separation, thus allowing to control the decrease of the permeate flux. Almost all the membranes in the separation cascades had severe fouling tendency, including even the final one.

In order to obtain the optimised regeneration of the membranes and the consequent high flux recovery, numerous chemical agents, such as NaOH, H_2O_2, EDTA, HNO_3, bleach, and alkali-acid treatment at different concentrations were tested. The regeneration with NaOH was performed in a bath, initially heated to 80°C, in which the membranes were dipped. The cleaning with all the other chemical agents was performed by recirculation inside the separation unit (CIP-cleaning).

Regarding the cleaning efficiency, NaOH proved to be very efficient, even though the cleaning would last, sometimes, for several days. The individual use of hydroxide solution was almost as effective, depending on the fouling caused by the separation material and membrane pore size. The individual use of acid gave a negative flux recovery. The cleaning cycle played an important role for the membrane regeneration and efficiency (Chang *et al.* 1994).

A systematic approach to the formulation of the optimal membrane cleaning strategy should lead to important process improvements, including optimised use of chemicals (minimising the environmental impact), reduced loss of the production time, improved permeate flux and quality control, extended lifetime of the membranes.

CONCLUSION

Ceramic three-channel membranes were applied to the treatment of stillage in various separation arrangements, where generally, the two step membrane arrangement is more convenient due to the operational costs reduction at the same separation efficiency. The membrane alignment and separation conditions were pivotal to the separation process.

The development of the separation process was unpredictable. The character of the separation material had a great impact on the membrane fouling. The membranes were very sensitive to the concentration polarisation and fouling effect.

Sufficient results were achieved in the arrangement of series using 0.2 μm membrane as the first step supplemented by the ultra-filtration membrane with 50 kDa membrane pore size. The most substantial differences were observed in the values of dry matter and COD as a marker of chemical pollution, both values having been reduced to 20% approximately.

The regeneration of the membranes was realised with various chemical reagents at different concentrations. The efficiency of sodium hydroxide depends more on the cleaning temperature than on the concentration. Hydrogen peroxide was effective only in the cleaning of the 150 kDa membrane.

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Corresponding author:

Ing. Kateřina Lapišová, Vysoká škola chemicko-technologická v Praze, Fakulta potravinářské a biochemické technologie, Ústav kvasné chemie a bioinženýrství, Technická 5, 166 28 Praha 6, Česká republika
tel.: + 420 220 445 016, fax: + 420 220 445 051, e-mail: katerina.lapisova@vscht.cz