



# Beer dealcoholization using pervaporation

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## Abstract

This work was aimed at laboratory testing of beer (and model solution) dealcoholization using pervaporation. Four commercially available membranes from the Sulzer company were tested. The modes of performed pervaporation tests were into the vacuum and into the stripping gas (N<sub>2</sub>). Pervaporation into the vacuum was observed to result in the precipitation of resin-like matter on the membrane permeate side. The performances of individual membranes are discussed in terms of selectivity and pervaporation fluxes.

**Key words:** pervaporation, dealcoholization, beer

## 1 Introduction

Production of non-alcoholic beer and low-alcohol beer is currently the fastest growing sector of brewing industry. The production of these kinds of beer in the Czech Republic amounts to about 2.7% of total beer production, similarly to other European countries (Basařová et al., 2010). The market with classical beer is more or less saturated but there are still many individuals who cannot consume alcoholic beverages for health, labor, religious or other reasons and the market with non-alcoholic and low-alcoholic beer is still increasing (Table 1) (Basařová, 2005). If non-alcoholic beer reaches the taste properties of normal beer, it can be expected that part of the classical beer drinkers will move to this non-alcoholic beer community.

In terms of European Union legislation, non-alcoholic beer has an alcohol content below 0.5% vol. and low-alcoholic beer from 0.6 to 1.2% vol. In the USA and Canada, products with alcohol content lower than 0.5% vol. cannot be labeled as beer but as a light malt beverage. In Japan, these beers are called beer taste drinks (Basařová et al., 2010).

The principles of non-alcoholic and low-alcohol beer production can be divided into two groups: techniques in-

cluding modification of the brewing process or feedstock and the methods entailing removal of alcohol from normal brewed beer. The first group includes methods with modification of the brewing process and the raw materials, which reduce the formation of alcohol already during the production. These procedures include the use of malts with low content of fermentable sugars, the mixing of beer with unfermented sweet wort or hopped wort, the use of the inhibitory effect of pressure on the yeast propagation and metabolism, the boiling of young beer after main fermentation, the immobilization of yeast and the use of special yeast strains (Basařová et al., 2010; Basařová, 2005).

Methods for removing alcohol from beer made in the conventional way can be further divided into membrane and other methods. The other methods include thin film distillation, fluidized carbon dioxide extraction, spray drying and subsequent dilution with degassed water, fractional crystallization or lyophilization (Basařová et al., 2010; Basařová, 2005).

Membrane processes that can be considered for removal of alcohol from beer are reverse osmosis, dialysis, nanofiltration and pervaporation (Jastřembská et al.,

2017; Salehi F. 2014). In the tasting tests, non-alcoholic beer produced by the removal of alcohol from normal beer was evaluated better than beers with a stopped (restricted) fermentation (Zuffal and Wackerbaucher, 2000a; Zuffal and Wackerbaucher, 2000b).

Pervaporation is a membrane separation process in which liquid mixtures are separated by their partial evaporation through a nonporous polymeric membrane. Pervaporation is divided into vacuum (under reduced pressure), and pervaporation into stripping gas. The inlet liquid is in direct contact with the surface of the membrane and the permeate (pervaporate) is removed in the vapour phase from the opposite side of the membrane. The driving force is the chemical potential gradient, namely the gradient of partial pressure of the component preferentially permeating through the membrane. The final composition of pervaporate is determined in particular by the solubility and diffusion coefficients of the input components in the membrane material, and can be very different from the vapor phase composition at liquid vapor equilibrium (Izák and Žák, 2014). Pervaporation has been also tested for the recovery of beer flavors to no-alcohol beers (Paz et al., 2017).

## 2 Materials and methods

### 2.1 Tested membranes

Flat hydrophilic and organophilic membranes from the Sulzer company were tested (Table 2).

### 2.2 Equipment

The tests were carried out on a laboratory equipment composed of a glass reactor with duplicator. The solution for dealcoholization was poured into the glass reactor and a module with the membrane was immersed in the vessel. The module has two inputs, one for the supply of stripping gas and the other for piping the pervaporate away (Figure 2). The input of stripping gas was closed while pervaporation into the vacuum tests was performed (point A in Figure 1). The pervaporate output was introduced into the cold trap, which was immersed in liquid nitrogen. The outlet from the cold trap was connected to a vacuum pump. In case of pervaporation into the stripping gas the outlet was opened to the atmosphere at point B (Figure 1).

A ring with a diameter of 3 cm was cut out of the membrane. After placing the ring membrane into the module it has an active area of 2.4316 cm<sup>2</sup>. In case of pervaporation into the vacuum, the absolute pressure on the pervaporate side was approx. 5 kPa.

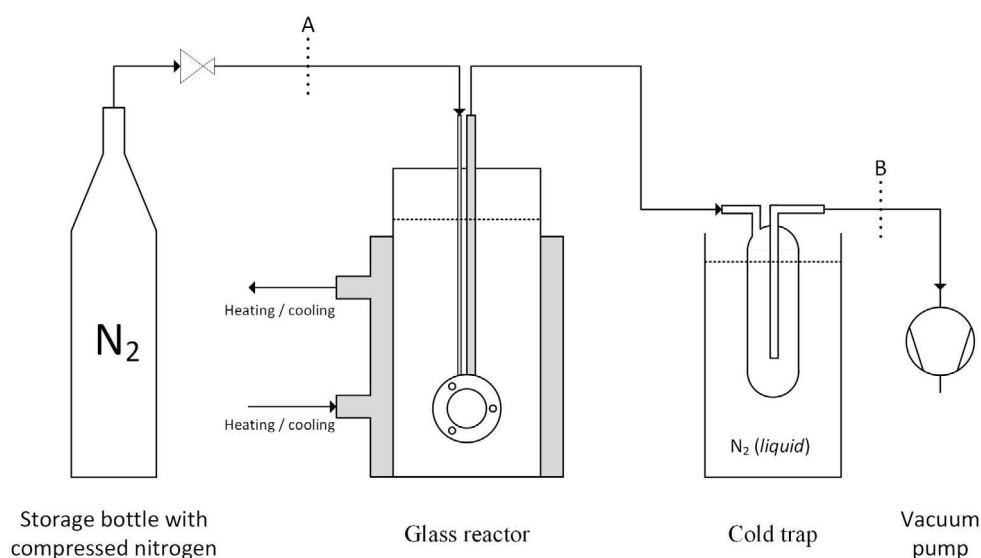
**Table 1** Volume of non-alcoholic and low-alcoholic beer production in Czech Republic

Year	Volume of production* [thous. hl]	Year-on-year increase [%]	Share on beer market [%]
2000	117		0.65
2001	135	15	0.76
2002	152	13	0.83
2003	166	9	0.9
2004	202	22	1.08
2005	239	18	n/a
2006	328	37	n/a
2007	497	52	n/a
2008	579	16	n/a
2009	534	-8	2.69*
2010	547	2	2.93*
2011	582	6	3.13*
2012	524	-10	2.74*
2013	494	-6	2.52*
2014	445	-10	2.27*
2015	472	6	2.35*
2016	555	18	2.71*
2017	578	4	2.84*

\*Courtesy of CZECH BEER AND MALT ASSOCIATION

**Table 2** Description of the membranes

Membrane	Type	Production batch	Material	Hydrophobicity	Specifying according to manufacturer
PERVAP™	4060	2972	PDMS	organophilic	for concentrating organic compounds from water solutions
PERVAP™	4155-30	3052	PVA	hydrophilic	for removal of methanol and water from organic mixtures
PERVAP™	4155-80	2781	PVA	hydrophilic	
PERVAP™	1256	2176	PVA	hydrophilic	

**Figure 1** Diagram of the apparatus

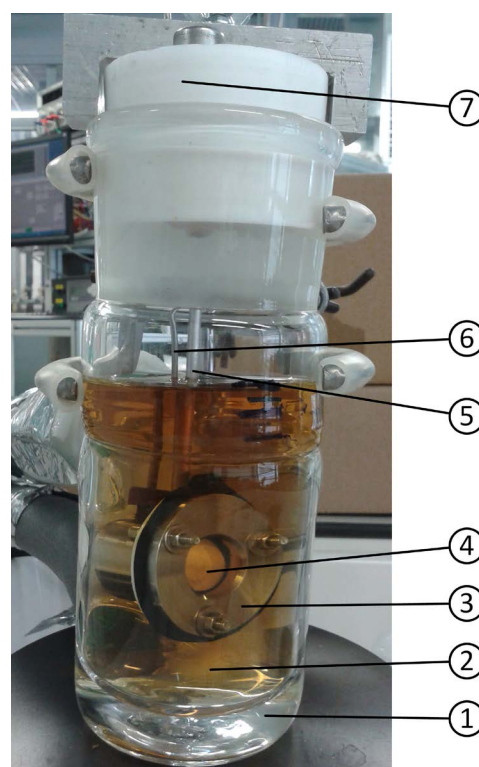
### 2.3 Test schedule

Nine experiments were carried out with four different membranes, on beer (Staropramen 10°, one production batch, different bottles) and model solution, into vacuum or stripping gas (N<sub>2</sub>) at 25 and 37°C and the length of the experiments 16–71.4 hours. A summary overview of the tests is presented in Table 3. The flow rates of the carrier gas (nitrogen) are approximately calculated from the pressure drop in the bottle.

### 2.4 Analytical evaluation

Analyses of alcohol were performed according to European Brewery Convention method “Alcohol in Beer by Near Infrared Spectroscopy” (EBC 9.2.6) on NIR beer alcolyzer ME (Anton Paar, Graz).

**Figure 2** Laboratory apparatus (1 – glass reactor with duplicator, 2 – stirrer, 3 – module for attaching the membrane, 4 – membrane, 5 – tube for connection to a freeze dryer and vacuum pump, 6 – tube for supplying the carrier gas, 7 – Teflon bung)



**Table 3** Test overview

Test No.	Membrane	Solution	Arrangement	Temp. [°C]	Time [hour]
1	4060	beer	vacuum	25	71.4
2	4155-80	beer	vacuum	25	48
3	4155-30	beer	vacuum	25	42
4	4060	water + ethanol	vacuum	25	46.5
5	1256	beer	vacuum	25	45.1
6	4060	beer	carrier gas (185 l/h)	25	16
7	4060	beer	carrier gas (123 l/h)	37	16
8	4155-80	beer	carrier gas (74 l/h)	25	20
9	4155-30	beer	carrier gas (49 l/h)	25	20

### 3 Results and discussion

Pervaporation flux, i.e. mass transfer across the membrane, and degree of enrichment are commonly used for evaluation of the pervaporation process.

Pervaporation flux is defined by the equation:

$$J_{pv} = \frac{m}{A \cdot t} \quad (1)$$

where  $m$  is the weight of the permeate which passes through the membrane area  $A$  in time  $t$ .

The degree of enrichment for preferentially permeating component A is defined by the equation:

$$\beta_A = \frac{w''(A)}{w'(A)} \quad (2)$$

where  $w'(A)$  is mass fraction of preferentially permeating component A in retentate and  $w''(A)$  is mass fraction of preferentially permeating component A in permeate. Samples of feed solution, retentate and permeate were taken and analyzed approx. every 24 hours (Table 4).

As seen in Table 4 and Figure 3 the decrease of ethanol concentration was only moderate during the experiments, and was significant only for the model solution (ethanol/water). A higher decrease was also observed in experiments with membrane 4060 and carrier gas. At the same time, in the 4060 N2 37 experiment we achieved the highest ethanol concentration in pervaporate of all experiments with beer in the feed (Figure 4) and the highest ethanol flux through the membrane (Figure 5). However, in this case the value of ethanol concentration in feed may be questioned because it differs significantly from other feeds. Considering that all samples originated from the same production batch, merely filling them into different bottles should not cause such variability. In some experiments the ethanol concentration in retentate even increased, indicating a faster water permeation through the membrane (e.g. 1256).

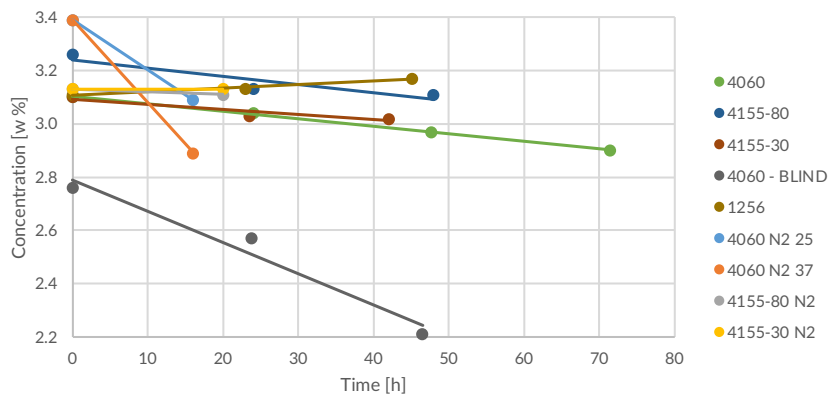
It is clear from both the course of ethanol concentration in retentate (Figure 3) and permeate (Figure 4) and the comparison of ethanol flux and the total mass flux through membrane (Figure 5 and Figure 6) that the membrane selectivities were low. This also proves the values of the degree of enrichment  $\beta_{EtOH}$  in Table 4.

A significant problem is the resin-like matter produced in the permeate side of the membrane (Figure 7) that blocks the permeation during vacuum pervaporation. Experts from the Research Institute of Brewing and Malting estimated that it could be made up of polyphenols and protein in addition to carbohydrates. It arises to a greater extent only during the first 24 hours, i.e. before the first sampling of longer tests. In the next period of time after cleaning during sampling it is not produced at all, or only minimally. The resin-like matter is formed only during pervaporation tests into the vacuum. It was partially formed during one experiment with a carrier gas when the gas flow decreased to about 49 l/h; this is probably not enough to runoff the vapor.

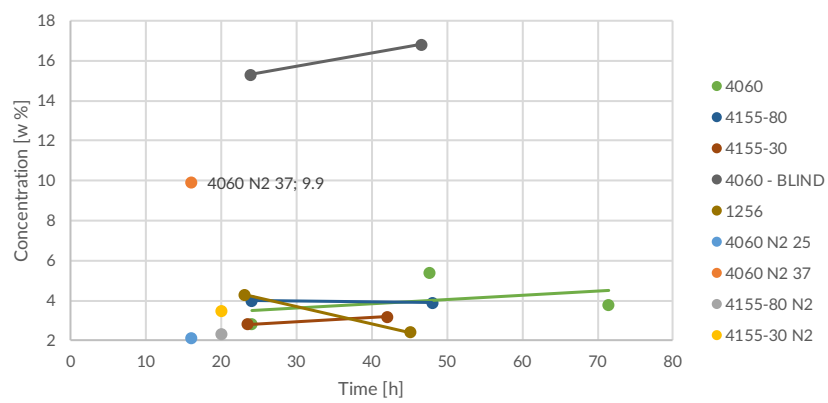
The production of the resin-like matter during the first period of experiments can explain the lower values of ethanol concentration in pervaporate in this period contrary to expectations and thus lower flow of ethanol at its higher concentration in the retentate.

For industrial application, blocking the membrane by deposition of resin-like matter can be eliminated by pervaporation to the carrier gas. At the same time, it is desirable to find a better membrane with improved separation properties in the water/ethanol system, in particular improved selectivity. Better separation of ethanol from other organic compounds will avoid the formation of the resin-like matter and losses of sensory important substances from beer to pervaporate.

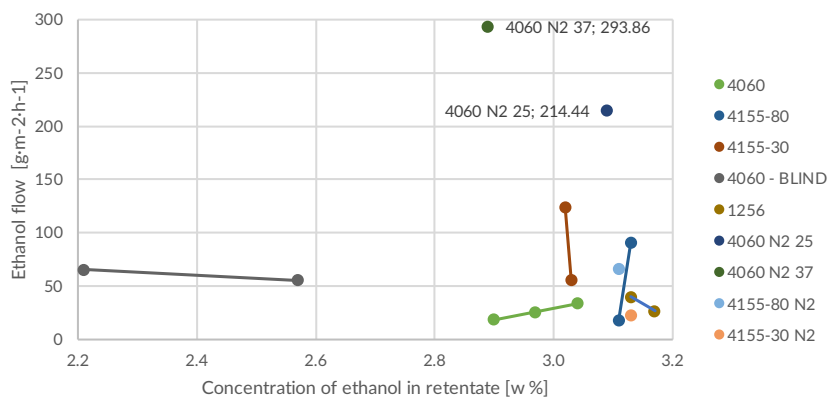
During pervaporation into vacuum we achieved a pervaporation flow of 50 g/m<sup>2</sup>/hr, which would correspond to membrane area of at least 540 m<sup>2</sup> for the treatment of 1 m<sup>3</sup> of beer per hour.



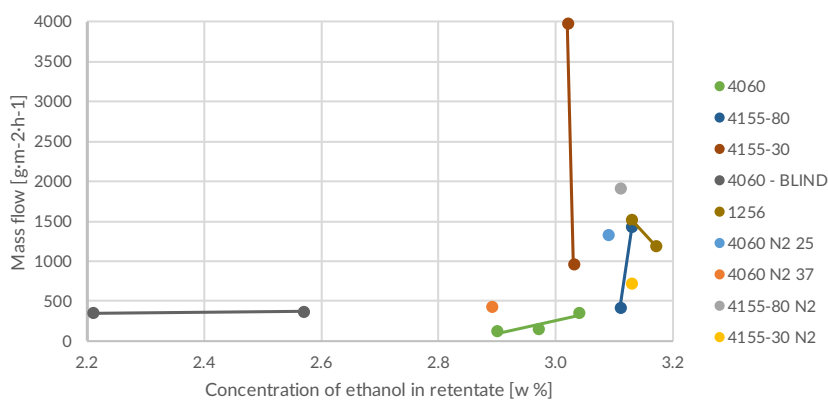
**Figure 3** Concentration of ethanol in retentate (beer) as a function of time



**Figure 4** Concentration of ethanol in permeate as a function of time



**Figure 5** Ethanol flow across the membrane as a function of mass concentration of ethanol in retentate



**Figure 6** Mass flux across the membrane as a function of mass concentration of ethanol in retentate

**Table 4** Analysis results and calculated fluxes and degree of enrichment

Test No.	Membrane/ comment	Time [hour]	$w'$ (ethanol) [wt. %]	$w''$ (ethanol) [wt. %]	$J_{ethanol}$ [g·m <sup>-2</sup> ·h <sup>-1</sup> ]	$J_{total}$ [g·m <sup>-2</sup> ·h <sup>-1</sup> ]	$\beta_{ethanol}$ [-]
1	4060	0	3.10				
		24	3.04	2.8	33.76	356.22	0.92
		47.7	2.97	5.4	25.24	150.37	1.82
		71.4	2.90	3.8	18.31	130.41	1.31
2	4155-80	0	3.26				
		24	3.13	4.0	91.01	1431.18	1.28
		48	3.11	3.9	17.97	413.52	1.25
3	4155-30	0	3.10				
		23.5	3.03	2.8	55.61	964.86	0.92
		42	3.02	3.2	123.79	3981.43	1.06
4	4060 BLIND	0	2.76				
		23.8	2.57	15.3	55.41	369.73	5.95
		46.5	2.21	16.8	65.19	351.33	7.60
5	1256	0	3.11				
		23	3.13	4.3	39.89	1515.67	1.37
		45.1	3.17	2.4	26.45	1192.71	0.76
6	4060 N <sub>2</sub> ; 25°C	0	3.39				
		16	3.09	2.1	214.44	1332.29	0.68
7	4060 N <sub>2</sub> ; 37°C	0	3.39				
		16	2.89	9.9	293.86	426.45	3.43
8	4155-80 N <sub>2</sub>	0	3.13				
		20	3.11	2.3	66.46	1912.98	0.74
9	4155-30 N <sub>2</sub>	0	3.13				
		20	3.13	3.5	22.39	715.21	1.12

$w'$  (ethanol) is mass fraction of ethanol in feed solution (beer),  $w''$  (ethanol) is mass fraction of ethanol in permeate,  $J_{ethanol}$  is partial pervaporation flux of ethanol,  $J_{total}$  is total pervaporation flux,  $\beta_{ethanol}$  is degree of enrichment for ethanol

During pervaporation into the carrier gas the pervaporation flow increased to a value as high as 200 g/m<sup>2</sup>/hr. Even so, it would take at least 135 m<sup>2</sup> of membrane area to process 1 m<sup>3</sup>/hr. Due to the low pervaporation flows and thereby a large membrane area it is the most appropriate to use modules with hollow fibres. The highest pervaporation flow was achieved by increasing the temperature to 37°C. In terms of brewing, however, it is not desirable to exceed 25°C for a longer period because it adversely affects the flavor.

Due to the relatively small volumes of produced pervaporate it should be

no problem with limiting the escape of volatile organic compounds. On freezing the pervaporate it would be possible to commercialize and sell it, for example as beer brandy, or as an extract, because it contains a significant amount of flavor compounds.

**Figure 7** The crystallized resin-like matter on the permeate side of the membrane

## 4 Conclusions

Under specific conditions the maximal ethanol concentration in the pervaporate was 16.8 wt. %; however, under real usable conditions it was a mere 5.4 wt. % and lower. Of the tested membranes, the PERVAP™ 4060 membrane made of polydimethylsiloxane (PDMS) has the best properties.

A resin-like matter formed in the first phase on the permeate side of the membrane during pervaporation arrangement into vacuum; this slowed down the process of separation. Mechanical cleaning does not come into consideration in the industrial application. For this reason the use of the hollow fiber in combination with pervaporation to vacuum is excluded.

To avoid the membrane clogging it is recommended to use a higher sweeping gas flow. Due to the low pervaporation flow and thereby a large required membrane area the use of modules with hollow fibres is the most appropriate.

## 5 Acknowledgements

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