

Application of Membrane Pervaporation Process to the Enhanced Separation of Fusel Oils*

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A commercial hydrophilic membrane, PERVAP-1001, was applied for the dehydration of natural fusel oils by membrane pervaporation. The fusel oils dehydrated to different levels (1.5 mass %, 5 mass %, and 9 mass % of water) by pervaporation as well as a raw fusel oil were subjected to batch fractional distillation. During pervaporation, a high selectivity of the investigated membrane toward water was found. The results of distillation showed that the fractionation of fusel oil containing less than 5 mass % of water yielded a much better separation of lower alcohols.

Fusel oil, a mixture of several alcohols (C₂ to C₅, mainly isoamyl alcohol) and water (up to 17 mass %) is a by-product in ethanol distilleries [1, 2]. These C₂—C₅ alcohols are considered as natural products, which confers them higher commercial value. Moreover, fusel oil can also be considered as a source of starting material for several natural flavours. Therefore, its utilization can make the ethanol production less polluting and more profitable. The fusel oil is nowadays processed by distillation in order to recover a mixture rich in pentyl alcohol isomers, while other alcohols are usually not recovered due to formation of azeotropic mixtures with water [1—3]. An effective recovery of C₂—C₄ alcohols requires the raw fusel oil dehydration prior to the final separation. Entrainer distillation with cyclohexane can be used for the fusel oil dehydration. However, this technique is energy- and time-consuming. Moreover, traces of cyclohexane can be found in the final products, thus limiting the use of C₂—C₅ fractions in the pharmaceutical and food industries [1, 2].

Pervaporation can be applied as an alternative technique for the fusel oil dehydration. Pervaporation is a membrane separation process in which a binary or multicomponent liquid mixture can be separated by a partial vaporization through a dense membrane [4, 5]. During pervaporation, the feed mixture is in direct contact with one side of the membrane, whereas

permeate is removed in a vapour state from the opposite side into a vacuum or sweeping gas and then condensed. Pervaporation can be used for dehydration of organic solvents, separation of binary organic compounds mixtures, extraction of organics from aqueous solutions, recovery of aromatic compounds in the food and cosmetic industry [6—8]. Moreover, it can be easily coupled with distillation into a hybrid process, just to enhance the resulting separation [9—11].

The aim of this study was to evaluate the viability of pervaporation as a dehydration step in the fusel oil fractionation process, followed by distillation.

EXPERIMENTAL

Pervaporation

Pervaporation experiments were carried out in the laboratory-scale pervaporation system described elsewhere [12]. A thermostated feed solution was circulated over the membrane by using a feed pump. The permeate was collected in cold traps cooled by liquid nitrogen. The upstream pressure was maintained at the atmospheric pressure during experiments, while the downstream pressure was kept below 100 Pa by using a vacuum pump. The permeate flux was determined by weighing, whereas the feed and permeate compositions were determined using a gas chro-

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Table 1. Initial Composition of the Fusel Oil Mixtures Subjected to the Fractional Distillation

Distillation	Composition of fusel oils/mass %						
	Water (b.p. = 64.5 °C)	Methanol (b.p. = 78.3 °C)	Ethanol (b.p. = 78.3 °C)	Propan-1-ol (b.p. = 97.3 °C)	2-Methylpropan-1-ol (b.p. = 108 °C)	Butan-1-ol (b.p. = 117.7 °C)	2-Methylbutan-1-ol 3-Methylbutan-1-ol (b.p. = 128–131 °C)
D1	13.77	0.02	9.03	0.33	14.00	0.20	62.65
D2	9.17	0.10	17.46	0.26	11.80	0.15	61.06
D3	5.09	0.11	18.25	0.27	12.28	0.15	63.85
D4	1.59	0.11	18.92	0.28	12.73	0.16	66.21

matograph (Varian 3300, Varian, USA). Fusel oils (provided by the Distillery “POLMOS” S.A., Kutno, Poland) containing 13–18 mass % of water were used as the feed mixtures. All experiments were performed at the temperature of 70 °C.

PERVAP-1001 hydrophilic membrane was used in this study (Sulzer Chemtech Membrane Systems, Neunkirchen, Germany). PERVAP-1001 membrane is a composite one and possesses an active layer made of crosslinked poly(vinyl alcohol), PVA. Performance properties of a given pervaporation membrane were defined by the separation factor α (eqn (1)) and permeate fluxes J [5].

$$\alpha_{\text{water/org}} = \frac{(w_{\text{water}}/w_{\text{org}})^{\text{permeate}}}{(w_{\text{water}}/w_{\text{org}})^{\text{feed}}} \quad (1)$$

where w_{water} and w_{org} are the mass fractions of water and organic components, respectively; *permeate* and *feed* superscripts describe the phases separated by the membrane.

Distillation

The fusel oils dehydrated to different levels (*i.e.* 1.5 mass %, 5 mass %, or 9 mass % of water) by pervaporation as well as the raw fusel oil were subjected to batch fractional distillation. The initial compositions of the separated mixtures are presented in Table 1. All distillation experiments were performed using a 12-theoretical plate column, under the atmospheric pressure, with the reflux ratio 1:20 while collecting foreruns and intermediate fractions and 1:10 while collecting main fractions. Temperature of the head of distillation column was measured every minute by using a quartz thermometer. The forerun fractions and interfractions were collected up to the temperature of 128 °C on the head of the distillation column. Samples of the fractions, taken during the distillation process, were analyzed using the gas chromatograph.

RESULTS AND DISCUSSION

The separation characteristics of the PERVAP-1001 membrane are presented in Fig. 1. Water was preferentially transported through the membrane,

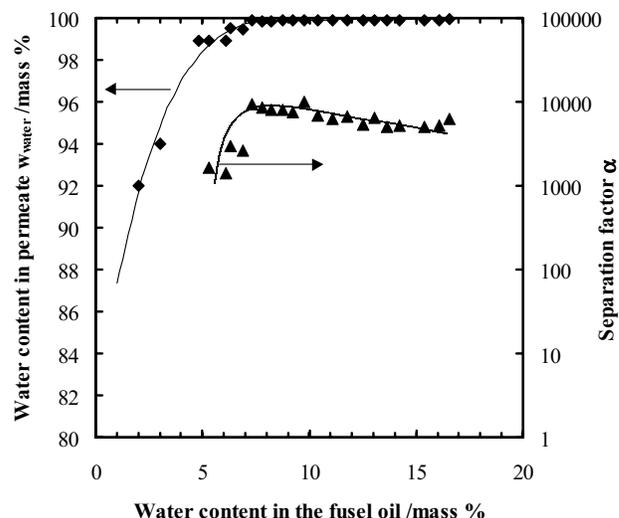


Fig. 1. Water content in permeate w_{water} and separation factor α vs. water content in the fusel oil.

yielding over 99 mass % of water in the permeate. This value was practically constant when the membrane contacted the feed mixtures containing more than 5 mass % of water. With decreasing amount of water in the feed mixture, the selectivity of membrane decreased slightly but the separation factor α remained very high, between 1000 and 8000. The selectivity drop was caused by the limited transport of methanol and ethanol through the membrane.

The final water content in the dehydrated fusel oil depended strongly on the dehydration process duration (Fig. 2). For the initial value of the feed volume per the membrane area equal to 118 dm³ m⁻² and the initial water content of 18 mass %, 30 h were needed to dehydrate fusel oils down to 5 mass % of water. Another 70 h were needed to decrease the water content below 1 mass % (over 90 % of the initial amount of water was removed from the feed mixture by pervaporation). It should be stressed that the pervaporation technique enables to achieve much lower water content, however, it would require much longer time of the separation or much larger area of membranes in the module.

The concentration dependence of the permeate flux (Fig. 3) was similar to that obtained with highly se-

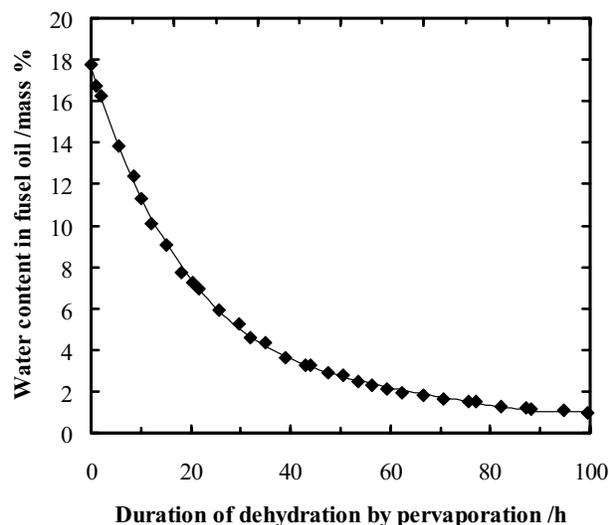


Fig. 2. Water content in the fusel oil *vs.* duration of the dehydration by pervaporation process. The ratio of initial feed volume to membrane area was $118 \text{ dm}^3 \text{ m}^{-2}$.

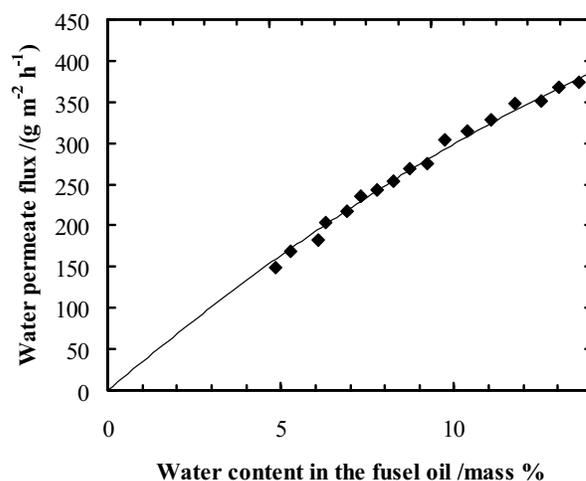


Fig. 3. Water permeate flux *vs.* water content in the fusel oil.

lective hydrophilic membranes [13]. The water content decline in the feed led to the reduction in both the driving force for the water transport and the swelling degree of the PVA selective layer. The transport of lower alcohols (*i.e.* methanol and ethanol) through the membrane decreased slightly with the water content decrease in the dehydrated mixture. In general, the flux of methanol and ethanol through the membrane

was very small ranging from 0.3 to $1 \text{ g h}^{-1} \text{ m}^{-2}$. Similar transport properties of PVA membrane were found for the batch dehydration of ethanol [13].

Results obtained during fractional distillation of fusel oils with different amount of water are presented in Table 2. The results of the distillation proved that the applied reflux ratios were sufficient to perform an efficient separation. Depending on the amount of wa-

Table 2. Results of the Fractional Distillation of Raw (D1) and Partially Dehydrated (D2, D3, and D4) Fusel Oil

Fraction	Distillation temperature/°C	Composition	Mass fraction/%			
			D1	D2	D3	D4
Forerun	20—78		2	0.9	0.9	0.9
Ethanol/Water	78.15		8	17.3	17	17.6
Intermediate fraction	78.2—89 ^a 78.2—108 ^b	Water	0.62	0.72	0.59	0.15
		Ethanol	0.75	0.62	0.73	0.83
		Propan-1-ol	0.17	0.12	0.14	0.25
		2-Methylpropan-1-ol	0.86	0.94	0.78	1.04
2-Methylpropan-1-ol/Water	89.8		23	13.9	6.2	—
Intermediate fraction	90—108 ^c 90—128 ^d	Water	0.15	0.04	0.11	—
		2-Methylpropan-1-ol	1.48	1.25	1.11	—
		Butan-1-ol	0.22	0	0	—
		2- and 3-Methylbutan-1-ols	1.25	0	0	—
2-Methylpropan-1-ol	108		—	4.5	9.53	14.34
Intermediate fraction	108.5—128	Water	—	0	0	0
		2-Methylpropan-1-ol	—	0.57	0.99	0.73
		Butan-1-ol	—	0.11	0.16	0.16
		2- and 3-Methylbutan-1-ols	—	1.20	0.97	0.79
Residue	> 128		61.50	57.83	60.79	63.21

a) Intermediate fraction collected during D1, D2, and D3 distillation; *b)* intermediate fraction collected during D4 distillation; *c)* intermediate fraction collected during D2, D3, and D4 distillation; *d)* intermediate fraction collected during D1 distillation.

ter in the initial mixture up to 8 different fractions (including fraction of isoamyl alcohols in the distillation residue) were obtained.

During the first distillation, D1 (the raw fusel oil composition shown in Table 1), only three main fractions were collected. Their composition corresponded to the azeotropic composition (Table 2). The last intermediate fraction was collected in a very wide range (89.3–128.4°C) and was composed mainly of 2-methylpropan-1-ol and 2- and 3-methylbutan-1-ols. The pentanols fraction contained also small amount of 2-methylpropan-1-ol and butan-1-ol.

The next distillation was performed with fusel oil containing 9.17 mass % of water (D2, Table 1). Because of the high water content in the fusel oil, the main fractions collected during the second fractional distillation, D2, were composed of water—alcohols azeotropic mixtures (see Table 2). Water content was too high to obtain pure 2-methylpropan-1-ol, so its main portion was distilled out in the form of water—alcohol heteroazeotrope. However, around 40 mass % of the initial amount of 2-methylpropan-1-ol was collected as a pure fraction. The last intermediate fraction was collected in a much narrower range (*i.e.* 108.3–129°C) compared to the previous distillation. 2- and 3-Methylbutan-1-ols fraction did not contain lower alcohols.

The fusel oil used for the third distillation, D3, contained 5.09 mass % of water (Table 1). At the beginning, forerun and ethanol fractions were received (Table 2). With respect to the lower water content compared to the previous distillations, the amount of 2-methylpropan-1-ol—water azeotrope taken at the temperature range of 89.3–89.5°C was much smaller. This fraction, after cooling, formed a two-phase system. The solubility of water in 2-methylpropan-1-ol (organic phase) and 2-methylpropan-1-ol in water (aqueous phase) was in a good agreement with the literature data [3]. The fraction of pure 2-methylpropan-1-ol (108.2–108.3°C) contained 78 % of the initial amount of this alcohol in the fusel oil. On the other hand, the distillation residue contained 95 % of the initial amount of 2- and 3-methylbutan-1-ols.

The last distillation experiment was performed with the fusel oil dehydrated by pervaporation down to 1.59 mass % of water (D4, Table 1). The low amount of water allowed to obtain only three main fractions (Table 2). The first one was composed of pure ethanol (with a very minor methanol impurity). The content of water in this fraction reflects the azeotrope composition. The next fraction contained 2-methylpropan-1-ol, with purity of 99.65 mass %. The third fraction was formed by the mixture of 2- and 3-methylbutan-1-ols, with purity of 99.95 % mass. Forerun and intermediate fractions constituted about 4.9 mass % of

the raw material used. The purity of the main fractions obtained allows their further use. The ethanol fraction could be returned to the rectification process. The other two alcohol fractions could be used as raw materials in the chemical, pharmaceutical, or food industries.

CONCLUSION

The experiments performed on the separation of fusel oils proved that a combined method (pervaporation followed by distillation) can compete with the entrainer distillation followed by the fractional distillation. The pervaporative dehydration of the raw material to a water content of 5 mass % is easy, fast, and cheap. The subsequent fractional distillation of dehydrated fusel oil leads to the alcohols fractions fulfilling the tough requirements of the pharmaceutical industry.

In general, the final efficiency of the fusel oil fractionation depends strongly on the water content in the distilled mixture. The lower the initial water content, the higher amount of pure 2-methylpropan-1-ol was recovered from the fusel oil. However, the raw material deep dehydration by pervaporation is a time-consuming process. Therefore, the optimal pervaporation-distillation procedure has to be found.

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