

ADVANCES IN RESEARCH AND TECHNOLOGY OF RAPESEED OIL

Monograph – part III



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COMPARISON OF VARIOUS TYPES OF PROTON-EXCHANGE MEMBRANES FOR THE RAPESEED OIL HYDROGENATION PROCESS

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Abstract

The polymeric proton-exchange membranes based on aromatic hydrocarbons (polyetheretherketone, polysulfone) were synthesized by post-sulfonation method. The membrane-cathode assemblies (MCAs) with those membranes were constructed and tested in the rapeseed oil hydrogenation process. It was found that MCAs made from these membranes give a low TFA content (0.4–1.5%), similarly as Nafion based MCAs. However, their durability should be improved.

Keywords: proton-exchange membrane reactor, rapeseed oil, oil hydrogenation, aromatic hydrocarbon membranes

INTRODUCTION

The employment of the proton-exchange membrane (PEM) reactor for the electrochemical partial hydrogenation of vegetable oils results in products with significantly lower levels of harmful *trans* fatty acids than in conventionally hydrogenated products [1]. However, this method, as well as the other ones, is not devoid of the disadvantages. One of them is relatively high cost associated, among others, with considerable price of the perfluorinated Nafion membranes that are typically used in the PEM reactors. For this reason, it is justified to search for other membrane materials, such as sulfonated aromatic hydrocarbon polymers, which could be used as substitutes for Nafion.

EXPERIMENTAL

SULFONATION OF POLYMERS AND MEMBRANE PREPARATION

Two commercially available polymers based on aromatic hydrocarbons were selected: polyetheretherketone (Victrex® PEEK 450PF) and polysulfone (PS, M_n 22 000, Sigma-Aldrich Poland) and sulfonated by post-sulfonation method.

Sulfonation of PEEK: The reaction was carried out according to [2]. 2 g of the dried polymer was dissolved in 50 cm³ conc. sulfuric acid at room temperature under vigorous stirring. Then the reaction mixture was brought to the desired temperature (20 or 40°C) and stirred for additional 3 h. After that time the product (sPEEK) was precipitated in an excess of cold water, filtered, washed several times with water and dried at 80°C for 24 h.

Sulfonation of PS: The reaction was carried out according to [3]. 7.2 g of the dried polymer was dissolved in 75 cm³ 1,2-dichloroethane (DCE) at room temperature under vigorous stirring. Then the reaction mixture was heated to the temperature of 60°C and the solution of 1.3 cm³ chlorosulfonic acid (CSA) w 15 cm³ DCE was added dropwise, during 1 h. The reaction mixture was stirred at 60°C for additional 2 h. After that time, the product (sPS) was filtered, washed several times with aqueous NaOH solution and water, and dried at 80°C for 24 h.

The dry polymer was dissolved (10–20 wt.%) in *N*-methyl-2-pyrrolidone (NMP), cast onto a glass plate and dried at 80°C for 48 h.

MEMBRANE CHARACTERIZATION

The proton conductivity σ (S/m) was calculated according to the following equation

$$\sigma = \frac{l}{R \cdot A} \quad (1)$$

where l , R , A are the membrane thickness (m), resistance (Ω) and area (m²), respectively.

The ion-exchange capacity (*IEC*) was determined using the titration method. The membrane samples in acid form were immersed in 1 M NaCl solutions for 24 h to replace H⁺ in the membrane by Na⁺. The H⁺, now in solution, were then titrated with 0.1 M NaOH. The *IEC* was calculated from

$$IEC = \frac{C_{NaOH} \cdot V_{NaOH}}{W} \quad (2)$$

where C_{NaOH} , V_{NaOH} are concentration (mol/dm³) and volume (dm³) of NaOH solution, respectively, W – mass of the dry membrane (kg).

The sulfonation degree (*SD*), was calculated from [4]:

$$SD \equiv \frac{\text{number of sulfonated mers}}{\text{total number of mers}} = \frac{M_p \cdot IEC}{1 - (M_f - M_p) \cdot IEC} \quad (3)$$

where M_p , M_f are the molar masses of the polymer repeat unit with and without functional group ($-\text{SO}_3\text{H}$), respectively. For PEEK $M_f = 0.390$, $M_p = 0.288$ kg/mol, for PS – 0.634, 0.532, respectively.

For the water uptake determination, the dry membranes were weighed and then soaked in distilled water at 25°C. After 24 h, the weight of wet membranes was measured. Water uptake ($W.U.$) was calculated as follows

$$W.U. = \frac{W_{wet} \cdot W_{dry}}{W_{dry}} \quad (4)$$

where W_{wet} and W_{dry} are the masses of wet and dried membrane sample, respectively.

OIL HYDROGENATION

Hydrogenation process was carried out in PEM reactor, shown schematically in Fig. 1. The main part of the reactor, membrane-cathode assembly (MCA), was prepared as follows: membrane (Nafion® 110 (DuPont, USA) or sPEEK or sPS) was stuck under a pressure to the stainless steel mesh (4 x 4,4 cm), 20 mg of Pd-black catalyst (Sigma-Aldrich Poland) was dispersed in membrane solution and coated on the wire mesh, on the opposite side in relation to the membrane.

During the process, water is electrolyzed at the anode to oxygen gas, hydrogen ions and electrons (5). The hydrogen ions flow through the cation-exchange membrane to the catalytically active cathode where they are reduced to hydrogen atoms (6) and added to the double bonds of unsaturated fatty acids present in the oil (7).

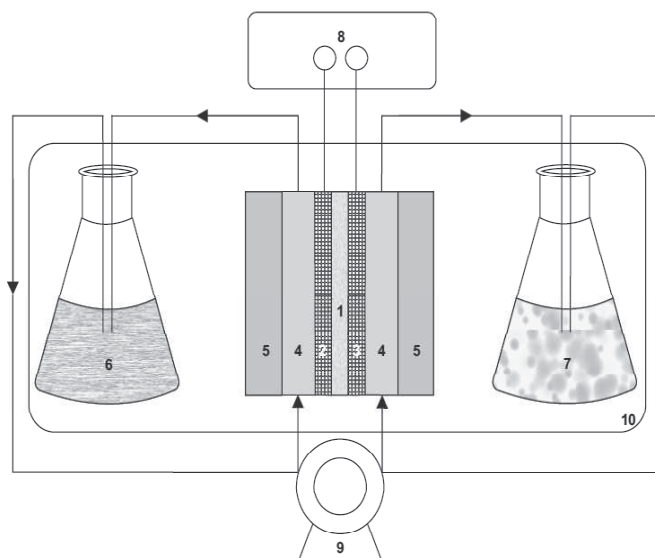


Figure 1. Scheme of the experimental setup. 1 – proton-exchange membrane; 2 – Pt mesh anode; 3 – cathode; 4 – plate with patterned flow channels; 5 – thermostating block; 6 – 0.05M H_2SO_4 ; 7 – rapeseed oil; 8 – power supply; 9 – pump



Our experiments were carried out during the period of 5 h, at the temperature of 60°C and the current density of 26 mA/cm². The oil with a composition as shown in Tab. 1 was supplied by Z.T. Kruszwica S.A.

Table 1. Fatty acids composition of rapeseed oil before hydrogenation

Fatty acid	C 14:0	C 16:0	C 16:1	C 18:0	C 18:1	C 18:2	C 18:3	C 20:0	C 20:1	C 22:0	C 22:1
Contents (%)	0.07	4.45	1.07	1.82	60.93	19.21	9.53	0.64	1.47	0.34	0.47

PRODUCTS ANALYSES

Fatty acid compositions of the initial oil and the partially hydrogenated products were determined by gas chromatographic analysis. The iodine value (*IV*) was calculated from the composition obtained by GC analysis using Eq. (8) [5].

$$\begin{aligned} IV = & (\% \text{ hexadecenoic acid} \times 0.950) + (\% \text{ octadecenoic acid} \times 0.860) \quad (8) \\ & + (\% \text{ octadecadienoic acid} \times 1.732) + (\% \text{ octadecatrienoic acid} \times 2.616) \\ & + (\% \text{ eicosenoic acid} \times 0.785) + (\% \text{ docosenoic acid} \times 0.723) \end{aligned}$$

RESULTS AND DISCUSSION

MEMBRANE PREPARATION AND CHARACTERIZATION

As shown in Fig. 2 and Fig. 3, the sulfonation of PEEK with H₂SO₄ as well as the sulfonation of PS with CSA are both the electrophilic substitution reactions, in which the sulfonic groups are introduced at the electron-rich sites of the polymer backbone, that is at the *ortho*-position to the ether linkage.

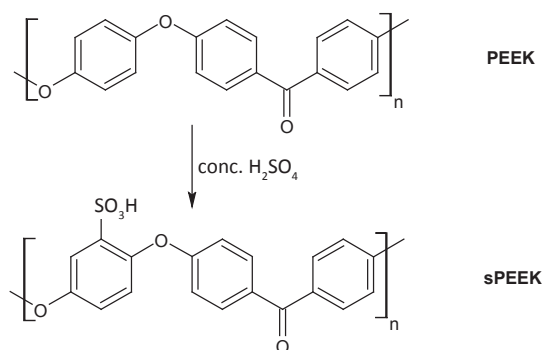


Figure 2. Sulfonation of PEEK

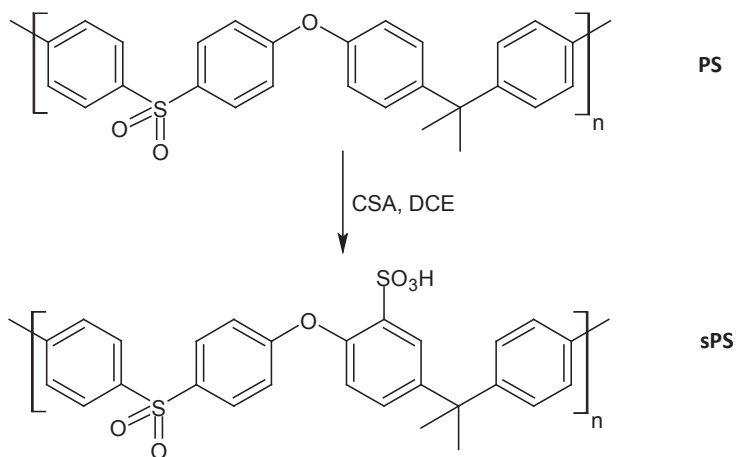


Figure 3. Sulfonation of PS

The main characteristics of the sPEEK and sPS membranes compared with Nafion 1100 membrane are reported in Tab. 2.

Table 2. Properties of membranes for PEM reactor

Membrane	<i>IEC</i> (mol/kg dry membrane)	<i>SD</i> (%)	σ at 25°C (S/m)	<i>W.U.</i> (kg water/kg dry membrane)
Nafion 1100	0.91 [6]	–	4.4	17
sPEEK 20	1.24	41	4.4	26
sPEEK 40	1.59	55	11.7	75
sPS	1.17	71	2.1	24

As can be seen, the ion-exchange capacity of all studied sulfonated aromatic hydrocarbon membranes is higher than *IEC* of Nafion.

The *SD* of sPEEK 20, which was obtained at the temperature of 20°C, is lower than *SD* of sPEEK 40 (obtained at 40°C) which confirms that the sulfonation process can be controlled by the reaction temperature. Consequently, the *IEC* and *W.U.* values are also higher for sPEEK 40 than for sPEEK 20.

The sPEEK 20 membrane showed the same high proton conductivity as Nafion 1100 membrane. As expected, increasing the degree of sulfonation of sPEEK membrane from 40 to 52% significantly increases the conductivity. The conductivity of sPS membrane is more than by half lower than conductivity of Nafion 1100 and sPEEK 20.

OIL HYDROGENATION

The selected results of a comparative study on the electrochemical hydrogenation of rapeseed oil in PEM reactor using various types of membranes are shown in Tab. 3.

Table 3. The results of the hydrogenation of rapeseed oil in PEM reactor

Membrane	<i>IV</i>	<i>TFA</i> (%)	MCA durability (h)
Nafion	98	0.6	30
Nafion	99	1.4	
Nafion	103	1.0	
sPEEK 20	97	1.0	15
sPEEK 20	104	1.0	
sPEEK 20	100	1.1	
sPEEK 40	93	1.5	15
sPEEK 40	103	0.4	
sPEEK 40	101	0.6	
sPS	102	0.5	5
sPS	99	0.9	

As it is seen, the iodine values of the partially hydrogenated products, as well as the *trans* fatty acids contents, are comparable to each other. Besides, the TFA content was found to be significantly lower (0.4–1.5%) compared to the traditional method (20–30%) at the similar iodine value of product [7]. Considering the results of the study on MCA durability under operating conditions, we observed that MCAs with sPEEK membranes are by half less durable than these with Nafion membrane while MCA with sPS membrane can be used for five hours only.

CONCLUSIONS

Low cost sulfonated aromatic hydrocarbon membranes (PEEK and PS) with ion exchange capacities in the range of 1.17–1.59 and proton conductivity in the range of 2.1–4.4 S/m can be simply fabricated by the post-sulfonation of the commercially available polymers and solvent casting of the polymer solution. MCAs made from these membranes can be used in PEM reactor for hydrogenation of a rapeseed oil with the comparable to Nafion MCAs results on the iodine value and *trans* fatty acids content. Further research will be focused on improving the durability of the prepared membranes, e.g. by blending with other available materials.

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