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Preparation, characterisation and evaluation of novel Ru- polyethersulfone (PES) catalytic membrane for selective hydrogenation of furfural to furfuryl alcohol

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S-1. Membrane characterization

S-1.1. Coating presence

The presence of the acrylic acid polymerized onto the membrane surface, after the UV-grafting, was identified by Frontier IR single- range system (Perkin Elmer).

S-1.2. Scanning Electron Mycroscopy (SEM)

The membrane morphology was observed by Scanning Electron Mycroscopy (Carl Zeiss SIGMA HD VP), studying the top layer and the cross section; the latter observed cutting the semple in liquid nitrogen. The samples were prepared for SEM analysis coating the one layer with carbon.

S-1.3. Ru content

The Ru quantification was evaluated by inductively coupled plasma optical emission spectrometry (ICP –EOS) analysis. The samples (1 cm^2 of membrane each) were dissolved in dimethyl formamide. The solvent was evaporated and then, an acid solution of aqua regia (HNO_3 wt. 70% / HCl 36% = 3/1 v/v) was added. The instrument (Perkin Elmer Optima 5300DV) dissociated the sample into atoms or ions, by ICP source, emitting them to radiation at a determinate wavelength, which are specific for each atom/ion. The concentration of Ru onto the membrane was expressed in $\mu g/cm^2$, by converting the values in μg/l obtained by ICP

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analysis. ICP analysis quantified the Ru amount in the solution constituted from the dissolved membrane. The Ru amount was calculated by knowing the concentration and multiplying it for the overall volume of the solution. The number obtained was dived for the membrane surface dissolved to obtain μg/cm^2.

S-1.4. TEM

Membranes samples, PES 220 nm not coated, PES 50, 220 and 800 nm coated and PES 220 coated after hydrogenation, were washed in acetone and embedded in Araldite. Ultrathin sections (60-90 nm thickness) were cut with a diamond knife, mounted on copper grids, and then examined with a JEOL JEM-1400 PLUS transmission electron microscope operating at 80 kV. EDS analysis was performed at 80 kV accelerating voltage, with a small spot size to ensure precise measurements.

S-1.5. Porosity

Membrane porosity was determinate by a gravimetric method, as reported in literature[1]. Dry membrane samples were weighed and impregnated in kerosene for 24h obtaining a completely filling of the voids. The total volume (V_{Tot}) is equal at:

$$V_{Tot} = V_m + V_v \qquad (s1)$$

Where V_m and V_v are membrane and void volume. Dividing for V_{Tot}, is possible to define the porosity, ε:

$$\varepsilon = \frac{V_{Tot} - V_m}{V_{Tot}} \qquad (s2)$$

Filling the void with kerosene the total volume will be the sum of volume of membrane and kerosene. By the density of each compound is possible to rewrite the eq. (s2) as:

$$\varepsilon = \frac{(W_w - W_D)/\rho_m}{(W_w - W_D)/\rho_m + (W_D/\rho_K)} \qquad (s3)$$

Where W_W, W_D, ρ_W and ρ_K are the weight of membrane dried and wet (filled with kerosene), density of membrane (1,37gr/cm^3) and kerosene (0.82 gr/cm^3) respectively.

S-1.6. Bubble point and pore size diameter

Bubble point, pore size distribution and diameter were determinate by PMI Capillary Flow Porometer (CFP1500 AEXL, Porous Material Inc, USA). Membranes sample were fully wetted with a solution of perfluorocompound Fluorinert-FC40 (16dynes/cm) for 24 hours[2]. The wet membrane allocated into a module at controlled N_2 pressurization; the method is based on gas permeation; at minimum Δp the N_2 starts to permeation through the membrane, emptying the pores from the liquid until full expulsion. The operating mode used was wet-up/dry-up and by the software Capwin the average pore size diameter is calculated via the interaction between the wet curve and the semidry curve, the last one obtained using the half slope of dry curve. By the Laplace equation [3] the pore size is possible to determinate:

$$\Delta p = \frac{2\gamma \cos\theta}{r} \qquad (s4)$$

Where Δp, γ, θ and r different of pressure, surface tension, contact angle (assumed equal at 0º) and pore radius.

S-1.7. Contact angle

The contact angle measures the surface interaction with three phase system (membrane/ water /air) [4]. Measurements were performed using ultrapure water (5µL) and estimating the angle between the membrane surface and the droplet; a low contact angle value (<90º) denotes a hydrophilic nature of the membrane. At the contrary, a high contact angle (>90º) indicates a hydrophobic nature. The contact angle was determinate by CAM200 (KSV Instrument LTD, Finland).

S-1.7.1. Mechanical tests

The tensile test measures the resistance of a material to a static or slowly applied force. The test was carried by ZWICK/ROELL testing machine (model Z 2.5) gripping opposite ends of the samples, with initial length 30 mm, and stretched at a constant controlled tensile speed until a predetermined stress [5].

S-1.7.2. Reaction test

The experimental setup is schematically in Figure s1, the gas streams were controlled by Brooks mass flow controller (MF-100 and MF-101) and the bio oil (or part of it) was fed by Eldex pump (P-100). Liquid and gas feeds were pre-heated before to input in the membrane reactor. The membrane reactor consists at flat stainless-steel module where the catalytic membrane (120 x 60 mm) was allocated, the temperature was maintained constant by a temperature controller (TIC-2) connected with a tape heating. The pressure into the 2 zones of membrane reactor were controlled by back-pressure controllers (BP-100 and BP-101). The output of membrane reactor before to analyse the-m, the liquid phase was collected in an ice trap system (S-100 and S-101). The liquid composition has been analysed by HPLC Agilent 1200 series with MS hook-up. After each reaction test the catalytic membrane was regenerated with a flow of H_2 and N_2 respectively 0.8 mL/min and 2.2 mL/min for 8 hours.

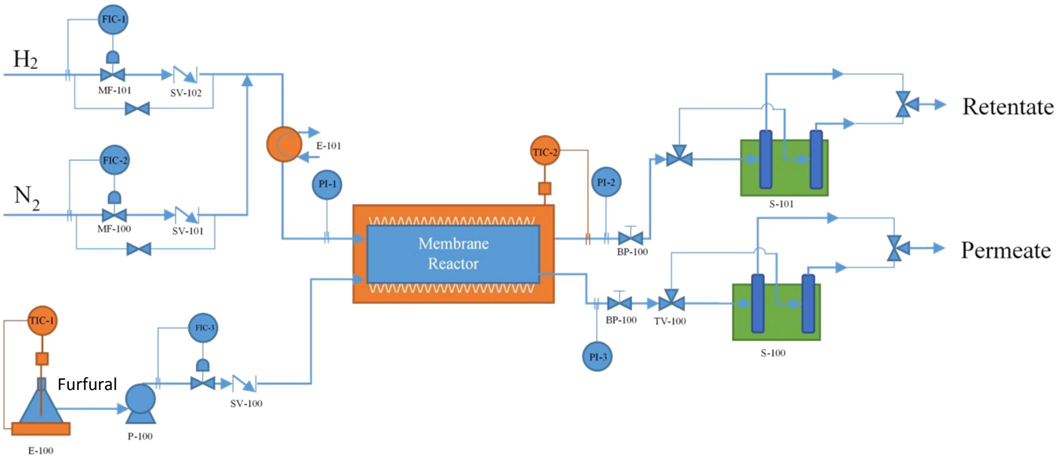
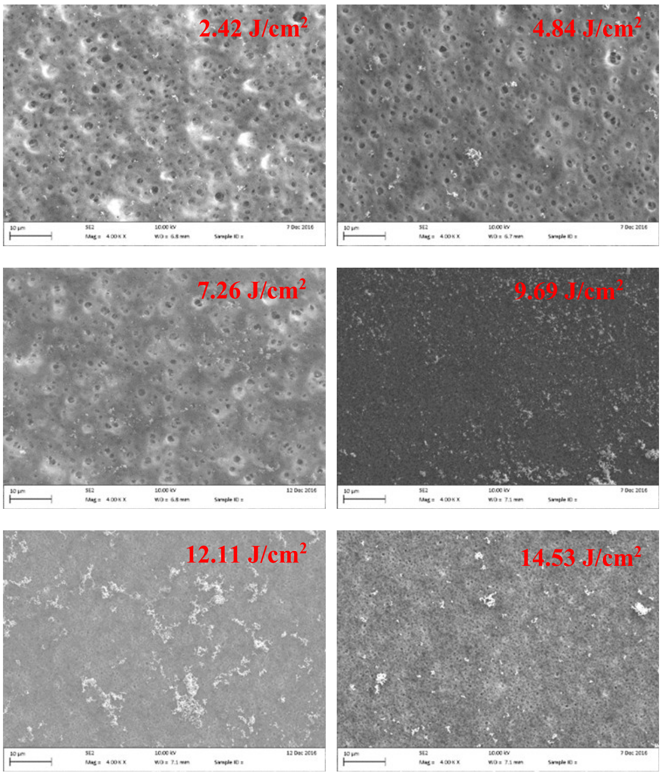


Figure s1. Lab-scale plant



SEM PES membrane 50 nm at different energy flux

Figure s2. SEM PES membrane 50 nm at different energy flux

Reference

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