Pervaporative dehydration of complex bioethanol using silica, hybrid and PVA membranes: study of permeation performances and effect of volatile organic impurities

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Keywords: Permeance, Pervaporation, Bioethanol dehydration, volatile organic impurities

Hydrophilic membrane pervaporation is largely described as a promising alternative to molecular sieves and azeotropic distillation, the ordinary techniques for ethanol dehydration (1). Three major types of membranes have been studied: i) organic (polymeric) membranes, ii) inorganic membranes and iii) hybrid membranes. Polymeric membranes remain the most widely used for pervaporation in the industry. These membranes are attractive because of their economical and fabrication advantages. During the last 10 years, considerable efforts have been put in the development of inorganic and hybrid membranes as they show a better chemical, hydrothermal and mechanical stability and are free of swelling.

Extensive research works have been focused on optimization of membrane material and operation parameters to maximize flux and water selectivity (2, 3). However, most of these works reported permeation data without systematically analyzing the contribution of the intrinsic parameters, *i.e.* membrane permeability (adsorption-diffusion through the membrane) and driving force. Moreover, in most cases, experiments were performed using ethanol that has undergone several distillations to remove volatile organic compounds (VOCs) impurities. Ethanol obtained from agricultural residues and lignocellulosic biomass contains high amount of impurities, mainly (VOCs). For example, the fermentation of grape marc produces bioethanol that contains up to 40000 ppm of methanol, some aldehydes, long chain alcohols and esters in smaller quantities, which can modify the perm-selectivity performances of pervaporation membranes.

This work aimed to study the performances of three pervaporation membranes: polymeric (PVA), inorganic (Me-Si[®]) and hybrid (HybSi[®]) used for ethanol dehydration. These membranes were compared in terms of permeance, flux and selectivity using pure, binary (ethanol + water), ternary (ethanol + water + methanol) and complex (grape marc bioethanol) mixtures. Emphases have been put on drag and competitions effects involved between molecules depending on feed mixture complexity.

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