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ScienceDirect
Journal of Membrane Science 308 (2008) 230–241
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Hydrophobic zeolite–silicone rubber mixed matrix membranes for ethanol–water separation: Effect of zeolite and silicone component selection on pervaporation performance

Leland M. Vane *, Vasudevan V. Namboodiri [1], Travis C. Bowen [2]

National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268 USA

Received 4 April 2007; received in revised form 27 September 2007; accepted 1 October 2007
Available online 9 October 2007

Abstract

High-silica ZSM-5 zeolites were incorporated into poly(dimethyl siloxane) (PDMS) polymers to form mixed matrix membranes for ethanol removal from water via pervaporation. Membrane formulation and preparation parameters were varied to determine the effect on pervaporation performance including siloxane chain length, crosslinking agent concentration and density of reactive groups, catalyst level, solvent type, zeolite type and loading, mixing method, and presence of a porous support membrane. Uniform dispersion of zeolite was critical to the achievement of reproducible results and ultrasonication with a probe-type device was found to be effective at particle dispersal. Properties of the vinyl-terminated PDMS and methyl-hydride crosslinking agents in the polymer system had a limited effect on performance while zeolite loading had the greatest effect. The highest observed selectivity of 3.0 was observed with 65 wt% zeolite loading, the highest practicable loading for the polymer system studied. The current results are placed in the context of ZSM-5/PDMS mixed matrix membranes previously reported in the literature for ethanol–water separation.
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Keywords: Mixed matrix membrane; Ethanol; Silicalite; Biofuel; Silicone rubber

1. Introduction

Separation processes based on permselective membranes are emerging as attractive options for various industrial separations. In order for membrane processes to be economically competitive with conventional separation processes, membranes with high flux and/or high selectivity are needed, due to the high efficiency of the traditional processes. Selective removal of ethanol from fermentation broth/water is such a challenge that would greatly benefit from more robust membrane materials having higher selectivities and permeabilities. Most biomass-to-ethanol conversion processes involve the fermentative production of ethanol from sugars released from the biomass. Depending on the biomass source and hydrolysis procedures, the concentration of ethanol in the fermentation broth can range from 1 to 15 wt%. Thus, in order to produce fuel-grade ethanol, the water content must be reduced from 85 to 99 wt% to less than 1.3 wt% water [1]. Distillation is the traditional technology for performing the bulk separation of ethanol from these dilute biomass fermentation broths with molecular sieve adsorption used to remove water down to fuel-grade levels. Pervaporation with ethanol-selective membranes, the subject of this paper, is an alternative to distillation and may have energy and capital cost advantages, especially for smaller-scale systems [2].

One way of analyzing the efficiency of an ethanol recovery technology is to look at the energy required to recover a unit of ethanol product. The energy expended to recover ethanol via pervaporation can be estimated from the heats of evaporation of water and ethanol (2260 and 838 $kJ\,kg^{-1}$), the ethanol–water separation factor (β_{ew}), the feed concentration of ethanol, and the desired degree of recovery of ethanol from the liquid [2]. The

* Corresponding author. Tel.: +1 513 569 7799.
E-mail address: Vane.Leland@epa.gov (L.M. Vane).
[1] Present address: Waste Management and Research Center, 1 E. Hazelwood Dr., Champaign, IL 61820, USA.
[2] Present address: UOP LLC, 25 E. Algonquin Rd., Des Plaines, IL 60017, USA.

0376-7388/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.memsci.2007.10.003

separation factor is the parameter traditionally used to describe the quality of separation performed by a pervaporation membrane. The separation factor of species 1 relative to species 2 (β_{12}) is defined as the ratio of the ratio of permeate compositions (C^V) to the ratio of the feed compositions (C^L) as follows:

$$\beta_{12} = \frac{C_1^V/C_2^V}{C_1^L/C_2^L} = \frac{J_1/J_2}{C_1^L/C_2^L} \tag{1}$$

where J_i is the flux of component i. Another, and more preferred, measure of separation quality is selectivity (α_{12}) which is the ratio of the permeabilities of the two species through the membrane, P_1 and P_2 with units of kmol m m^{-2} s^{-1} kPa^{-1}:

$$\alpha_{12} = \frac{P_1}{P_2} \tag{2}$$

In situations where the actual thickness, δ, of the membrane is not known or where multilayer membranes are used, permeances can be used instead of permeabilities in Eq. (2). Permeance is the driving force normalized flux, which is P_i/δ for single layer membranes.

In Fig. 1, energy requirement estimates for 95% ethanol recovery by pervaporation for β_{ew} of 8, 10, 20 and 50 are shown for a feed ethanol concentration range of 1–5 wt%. For comparison, energy requirements for large-scale, heat-integrated distillation systems reported in the literature, which assumed a fixed residual concentration of ethanol of 0.02 wt%, are also shown [3,4]. The heat of combustion of ethanol is shown as a reference line. For this hypothetical scenario, membranes with β_{ew} greater than 20 are required to yield the same energy efficiency as distillation. Ethanol recoveries lower than 95% would allow the use of less selective membranes while higher ethanol recoveries would necessitate more selective membranes.

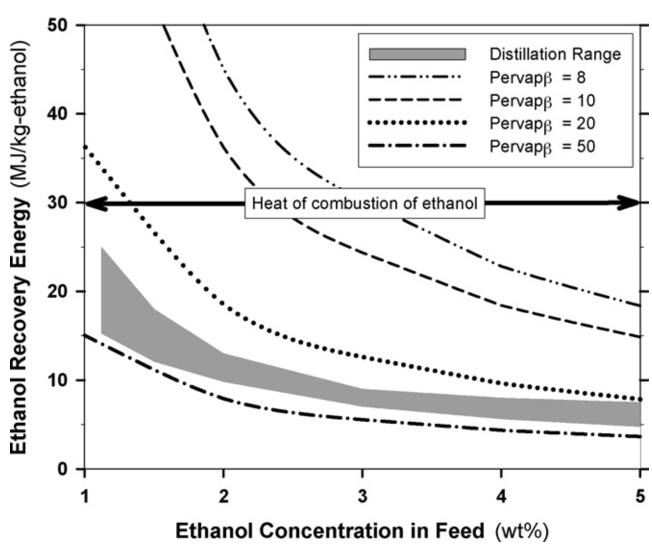

Fig. 1. Energy required to recover ethanol from water as a function of the ethanol concentration in the feed stream for two heat-integrated distillation systems and pervaporation systems at several ethanol–water separation factors. Distillation values from Ref. [4] (design "C") and Ref. [3]. Ethanol recovery of 95% assumed for pervaporation while both distillation scenarios treat residual to 0.02 wt% ethanol. Product purity is 93 wt% ethanol.

The standard reference hydrophobic membranes for ethanol removal from water are constructed with silicone rubber (SilR) as the selective layer. Silicone rubber has a higher flux and ethanol–water selectivity than most other hydrophobic ethanol-permeable polymers. The reported ethanol–water separation factor for "pure" silicone rubber membranes ranges from 4.4 to 14.4 with an average of about 7–8 [2]. These values are well below the target of $\beta_{ew} > 20$ for the scenario illustrated above. Thus, in order to improve the energy efficiency of pervaporation for ethanol recovery from water, membranes with selectivities greater than that of silicone rubber are needed. Based on a review of the pervaporation literature, inorganic membranes with a ZSM-5 zeolite selective layer in which the Si:Al ratio is high (HiSiZ), particularly silicalite-1, are capable of delivering separation factors up to 125 (based on results with a PDMS-sealed silicalite-1 layer, even higher separation factors may be possible for defect-free silicalite-1 layers) [2]. Mixed matrix membranes consisting of HiSiZ zeolite particles dispersed in silicone rubber have been shown to deliver β_{ew} values as high as 59 [2]. The expected ease of manufacturing and reduced cost of the mixed matrix membranes relative to zeolite membranes, combined with the ability to achieve values of β_{ew} necessary to save energy relative to distillation makes these materials attractive.

The incorporation of zeolite particles in polymer membranes might seem like a straightforward undertaking. However, a survey of the HiSiZ–SilR mixed matrix literature shows that this seemingly simple operation does not always yield the highest performing membranes. For example, as stated above, the maximum reported value of β_{ew} for a HiSiZ–SilR mixed matrix

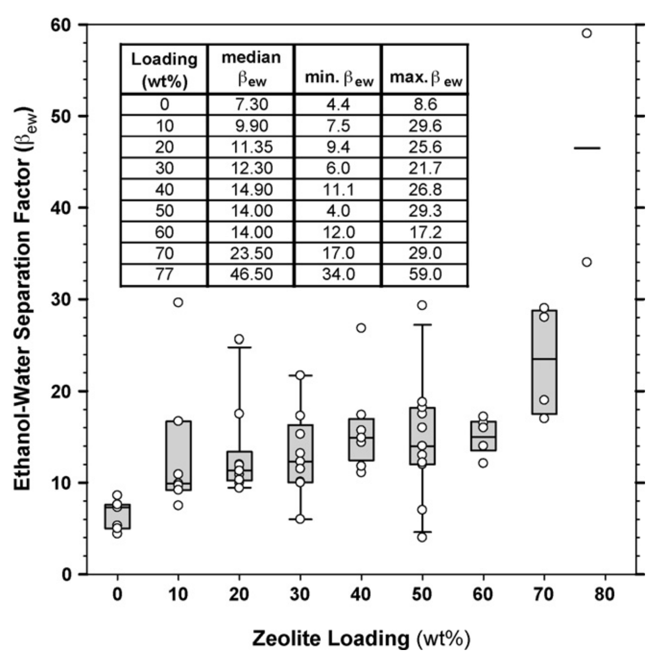

Fig. 2. Ethanol–water separation factors reported in the literature for high silica ZSM-5 zeolite–silicone rubber mixed matrix membranes [5–13]. Reported temperatures range from 22 to 50 °C, ethanol feed concentrations ranged from 4.4 to 7 wt%, membrane thicknesses ranged from 4 to 500 μm. Open circles represent all data points used in the analysis. Boxes: lower bound = 25th percentile, upper bound = 75th percentile, inner line = median, whiskers represent 10th/90th percentiles when 9 or more data points available.