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INVESTIGATIONS ON THE APPLICATION OF PERVAPORATION PROCESSES WITHIN THE LIGNO-CELLULOSIC ETHANOL PRODUCTION SCHEME

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ABSTRACT

The production of ligno-cellulosic ethanol is gaining wide interest with the progressive depletion of fossil fuels. Pervaporation, which is a selective membrane separation process that consumes relatively low energy, is being proposed for utilization within the ethanol production scheme. This work is dedicated to investigations on the application of pervaporation using simulated solutions in two stages namely, concentration of ethanol during fermentation using hydrophobic polydimethylsiloxane (PDMS) spiral wound membrane and dehydration of high concentration ethanol using hydrophilic optimized silica membrane. A semi-pilot plant based on a novel conceptual process design combining both membranes to be used interchangeably has been developed. The hydrophobic PDMS system has been operated using spiral wound module of area 0.6 m^2 at a flow rate of 600 L/h and vacuum less than 0.1 mbar. Within the tested range of ethanol concentration, the flux ($g/m^2/h$) varied between 780 and 2300 with a maximum separation factor of 3.67. The tubular hydrophilic membrane of area 0.04 m^2 has been operated at a flow rate of 300 L/h and vacuum of less than 0.1 mbar. The flux and concentration have been measured during the experiments at suitable time intervals. At about 95% initial ethanol concentration, the flux ranged between 2700 and 3400 ($g/m^2/h$) and the separation factor reached about 122. For both operational modes, the results reflect optimum conditions for operation with maximum flux and acceptable separation factor. It is concluded that pervaporation proves to be a viable option for separation and dehydration of ethanol due to its technical performance and minimum energy usage.

Keywords: pervaporation, ethanol, concentration, dehydration, optimized silica, PDMS.

INTRODUCTION

Although biofuels have been produced since the World War II with the shortage of fossil fuels, it has not been further investigated until the World Energy Crisis in the seventies of the last century (http://biofuel.org.uk/history-of-biofuels.html). Since then, extensive efforts have been undertaken worldwide to develop technically and economically viable processes for the production of various optional biofuels. The production of ethanol from ligno-cellulosic materials is currently witnessing remarked progress. An essential step in the process is the concentration of ethanol which is produced at very low concentration from the fermentation stage to about 99%.

During the current decade, membrane-based pervaporation has emerged as an attractive separation technique. Numerous polymeric, inorganic and composite membranes have been developed for either recovering volatile species or removing water from aqueous-organic solutions. Pervaporative membrane concentration and dehydration techniques have potential for reduction of energy requirements and hence operating costs (Wijmans J. G. *et al*., 1995; Feng X. *et al*., 1997).

For recovery of ethanol from ethanol-water mixtures, silicon-containing polymers particularly PDMS and its derivatives have been often used due to their stable performance. Using PDMS membrane, Mohammadi *et al*. (2005) found that the membrane separation factor decreases with increase of ethanol feed concentration (Mohammadi T. *et al*., 2005). The same membrane has been also employed by Ishibara (1987) with ethanol feed concentration of 8% and a separation factor of 10.8 has been achieved (Ishibara K. *et al*., 1987). Other workers utilized PDMS membranes held on polymeric supports as polyimide (PI), polysulfone-polyethersulfone (PS-PESF), polysulfone-interpenetrating polymer network (PS/IPN) cellulose acetate (CA). Membranes of thicknesses ranging from 15 to 20 microns, apart from the 2-micron PDMS/CA membrane, were employed for ethanol feed concentrations ranging from 5 to 10% at feed temperatures of 30 to 60°C to obtain separation factors of 5.5-8.5 and corresponding fluxes of 0.16-0.019 kg (Kashiwagi T. *et al.*, 1988; Takegemi S. *et al*., 1992; Liang L. *et al*., 1996; Li L., *et al*., 2004). Higher separation factors and fluxes were obtained using the 30-micron PDMS-PPP (poly (1-phenyl-1-propyne) membrane which gave a separation factor of 40 and a flux of 1.3 kg/m^2 h at 7% ethanol feed concentration and 30°C (Nagase Y. *et al*., 1990), as well as the 104-micron PDMS-PVDF (poly-vinylidine fluoride) membrane which had a separation factor of 31 and a flux of 0.9 kg/m^2 h at 10% ethanol feed concentration (Chang C.-L. *et al*., 2004). PDMS membranes deposited on ceramic supports have been also employed mainly to enhance the mechanical properties of polymeric membranes. PDMS/ceramic composite membranes

generally have high fluxes since the ceramic support has high surface porosity and hence small transport resistance. Jia *et al.* (1992) used a PDMS/silicalite with a thickness of 20 microns to recover ethanol with a feed concentration of 5.1% at 22°C and they obtained a separation factor of 34 with a flux of 0.15 kg/m^{2}h. In addition, ZrO_2/Al_2O_3 supports were found to possess high flux and acceptable separation factor. For a PDMS/ ZrO_2/Al_2O_3 membrane of an average pore size of 0.2 microns, a flux of 19.5 kg/m^{2}h and a separation factor of 5.7 were obtained at 70°C and 460 Pa and an ethanol feed concentration of 4.3% (Xiangli F. *et al*., 2007). Improved performance has been obtained by incorporating zeolite particles into PDMS membranes (Zhan X. *et al*., 2009; Ji L. *et al*., 2015).

For the dehydration pervaporative membranes, the separation factor generally varies inversely with water permeability and flux. The selectivities of a PAA/PVA/GA membrane of effective area 39 cm^2 varied from 850 to 1950 at ethanol feed concentrations of 85% to 95% and corresponding fluxes of 2.16 to 0.043 kg/m^2 h, respectively (Namboodiri V. V. *et al*., 2005), whereas the selectivities of a 12 cm^2 ceramic silica membrane ranged from 50 to 160 at ethanol feed concentrations of 91-98% and corresponding fluxes of 0.35 to 0.15 kg/m^2 h, respectively. A recent trend is the preparation and application of ceramic supported graphene oxide composites for dehydration of ethanol water mixtures by pervaporation (Li G. *et al.,* 2014; Zhao J. *et al*., 2015)**.** The water concentration reached 39.92% with a flux of 0.462 kg/m^2 h at 40°C for a feed of 5% water.

In this paper, performance indicators of ethanol separation from water are investigated using PDMS hydrophilic and optimized silica dehydration membranes. The immediate objective is to rationalize design basis for scaling up purposes with emphasis on the operational limitations of this technology. Thus, a rather improved ethanol separation process is developed within the context of optimizing the lignocellulosic conversion into ethanol.

THE PROPOSED APPLICATION OF PERVAPORATION

The authors of this work have extensively studied technical and economic aspects of ethanol production from rice straw (Tewfik S. R. *et al*., 2010; 2011; 2013). The proposed application of pervaporation within the process of ethanol production from ligno-cellulosic materials essentially comprises concentration during the fermentation phase and dehydration of the produced ethanol to the required purity (greater than 99%). The integrated process is schematically presented in Figure-1 for sequential or simultaneous saccharification/fermentation. For the concentration stage, the pervaporation is applied for treatment of a side stream where a portion of the broth from the reactor is directed to an ultrafiltration unit. The retentate is returned to the reactor while the clear permeate is directed to the hydrophobic pervaporation unit to partially separate and collect the formed ethanol. The stream with the relatively low ethanol concentration is also returned to the reactor for further processing.

The addition of pervaporation within the ethanol production scheme provides higher yield of ethanol and shorter production duration through continuous extraction of ethanol from the fermenter to enhance the forward reaction of ethanol formation. Also, the use of pervaporation for dehydration of ethanol could provide a technical and economic feasible option competing with azeotropic distillation.

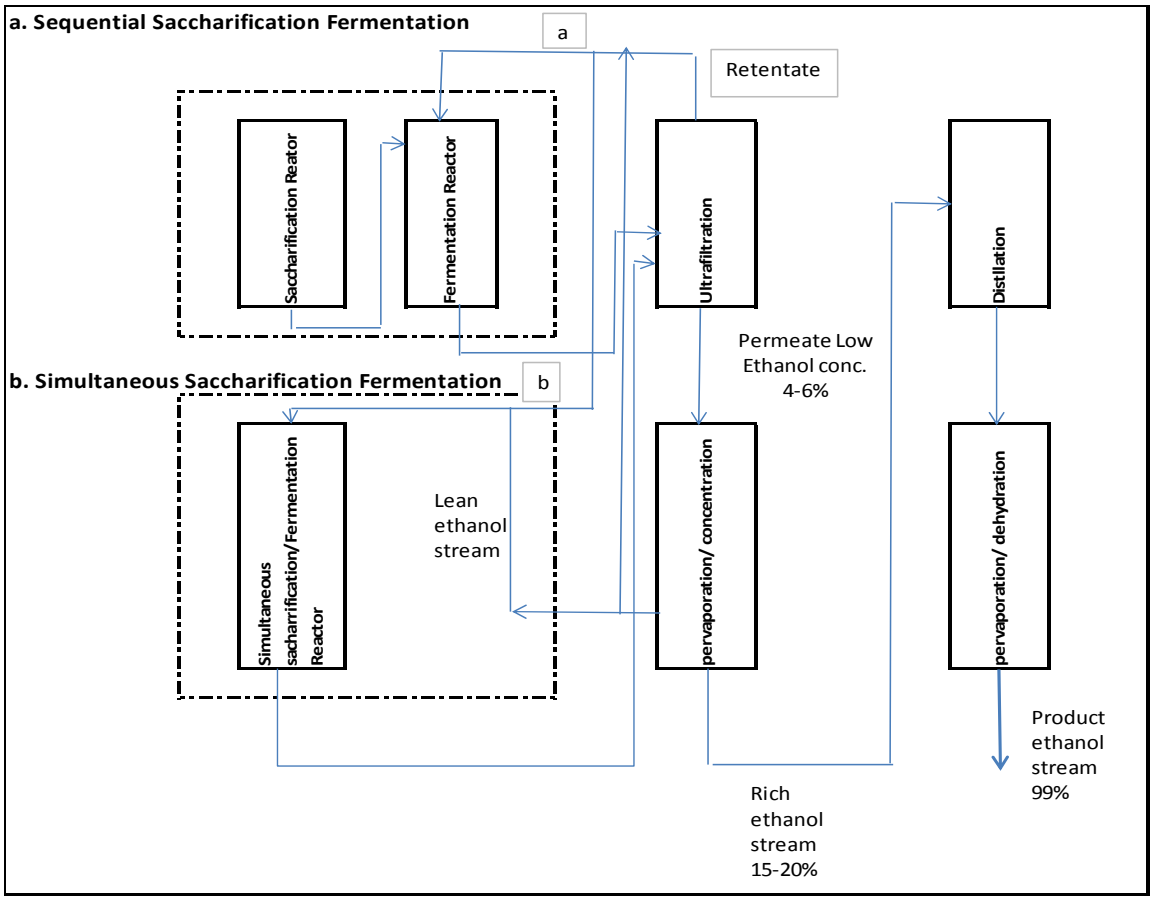

Figure-1. Proposed application of Pervaporation within the ligno-cellulosic ethanol production scheme.

EXPERIMENTAL INVESTIGATIONS

Experimental set-up

A semi-pilot plant experimental pervaporation set-up has been constructed and operated. The set-up is based on a novel conceptual process design combining both membranes to be used interchangeably which has been developed within the scope of this work. The modules and the detailed process design have been supplied by Pervatech (http://www.pervaporation-membranes.com). The hydrophobic/organophilic module is spiral wound PDMS of effective area 0.6 m^2. The hydrophilic module is tubular optimized silica selective membrane (Model PVM-043-500-4) of area 0.04 m^2. Details of the modules are provided at the website of the supplier. The experimental set-up is depicted in Figure-2.

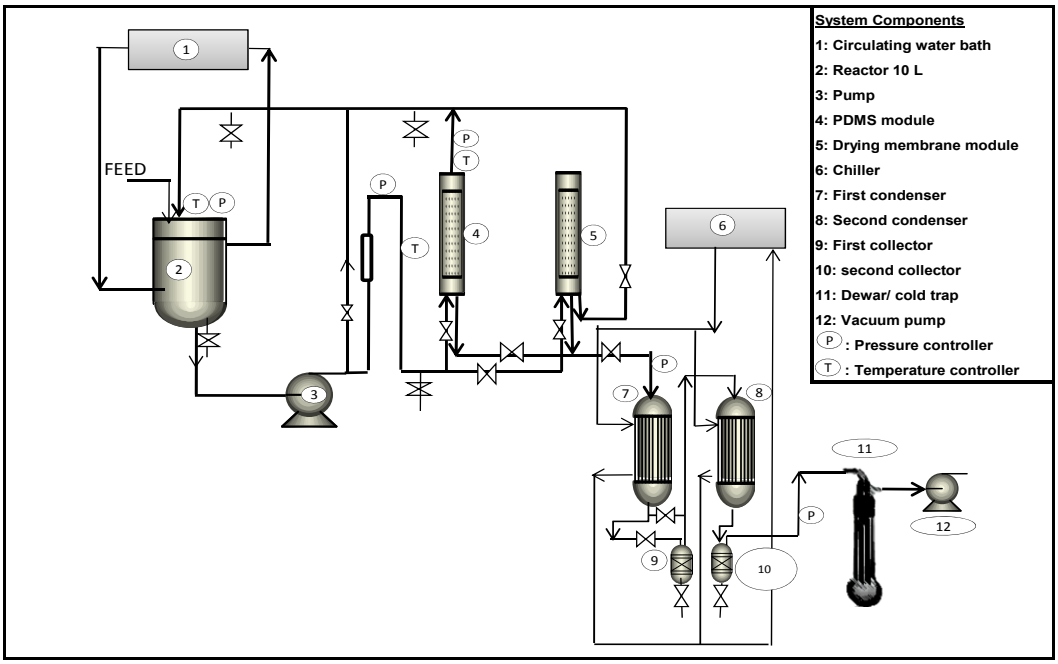

Figure-2. Flowsheet of the experimental pervaporation set-up (reproduced with permission of Pervatech).

In this system, the feed solution is fed to a 10-liter jacketed stainless steel tank which is heated using a temperature controlled circulating water bath (Polyscience), to the desired preset temperature. The heated solution is transferred by a centrifugal pump (Lowara) to the membrane module depending on the operational mode: concentration mode using the organophilic PDMS PV membrane module or dehydration mode using the hydrophilic optimized silica tubular membrane. The output is cooled through two sequential stainless steel 316 tubular condensers of total cooling area 0.25 m^2. Condensers are cooled using a chiller to a temperature of about 4^oC. The volatile vapors are further condensed in a 500 mL cold trap immersed in a Dewar Vessel (Sigma Aldrich) cooled with liquid nitrogen and connected to a vacuum pump (MTI Corp.) operating below 0.1 mbar. The system is provided with flowmeters, pressure and temperature indicators installed as depicted in Figure-2.

Experimental procedures

Two modes of operation are applied, the concentration and dehydration modes:

Concentration mode

The concentration mode is applied to simulate the separation of ethanol by pervaporation from the fermentation broth, after removing the cells by microfiltration and recycling it to the fermenter, to maintain the ethanol concentration in the fermentation broth at a low level which is minimally inhibitory to the fermenting organism (typically 3-6wt %) while raising the concentration of ethanol by pervaporation to 15-20%. Thus, a solution of ethanol - water of concentration in the range of 3-6 wt.% has been used throughout the experiments. The ethanol (ADWIC) is dissolved in distilled water. The system is first flushed at the desired temperature for 15 min at a flow of about 100 L/h using a dilute water ethanol solution. The system is then run for about 1 hour at the desired flow rate (about 600 L/h) and temperature (45^oC), applied pressure 1.3 bar and vacuum below 0.1 mbar to reach steady state. Samples of the permeate and recycled streams are then collected at appropriate time intervals, collected permeate volume measured and analyzed using a digital refractometer (CETI). The system is run for the desired time length (about 2-3h). At the end of the experiment, the mixture in the cold trap is collected, measured and analyzed.

Dehydration mode

The dehydration mode is adopted to raise the concentration of ethanol from 90-95% to over 99%, to be used as mixed with gasoline as E15 or higher. Experimental procedure rather similar to the Concentration Mode is adopted. The module used is the hydrophilic optimized silica membrane from Pervatech of area 0.04 m^2, operating temperature range is 60-70^oC, the feed pressure is about 2-4 bar and a vacuum of about 0.1 mbar. The system is then run for 3 hours at the desired flow rate (about 300 L/h).

Performance parameters

Conventional membrane parameters namely flux and separation factor have been adopted for performance assessment according to the following equations:

$$J=Q/At \quad (1)$$

Where J is the flux ($g/m^2/h$), A is the membrane area (m^2); t is time (h) and Q is the flow rate (L/h).

$$\alpha=(Y_w/Y_e)/(X_w/X_e) \quad (2)$$

Where α is the separation factor, Y is the weight fraction in permeate and X is the weight fraction in feed. Subscripts w and e refer to water and ethanol, respectively.

RESULTS AND DISCUSSION

Ethanol concentration via polymeric membrane

Experiments performed on the pilot-scale system described in this paper have been carried out at 45ºC. Clearly as shown in Figure-3, the flux increases both with temperature and ethanol feed concentration. The flux-concentration profile is linear at this temperature. This trend has been also reported by Mohammadi *et al*. (2005) using PDMS membrane at 30ºC, and by Zhou *et al*. (2011) for an ABE (Acetone-Butanol-Ethanol) feed mixture having 1 wt.% butanol, 0.5% acetone, and 0.15% ethanol at 50ºC.

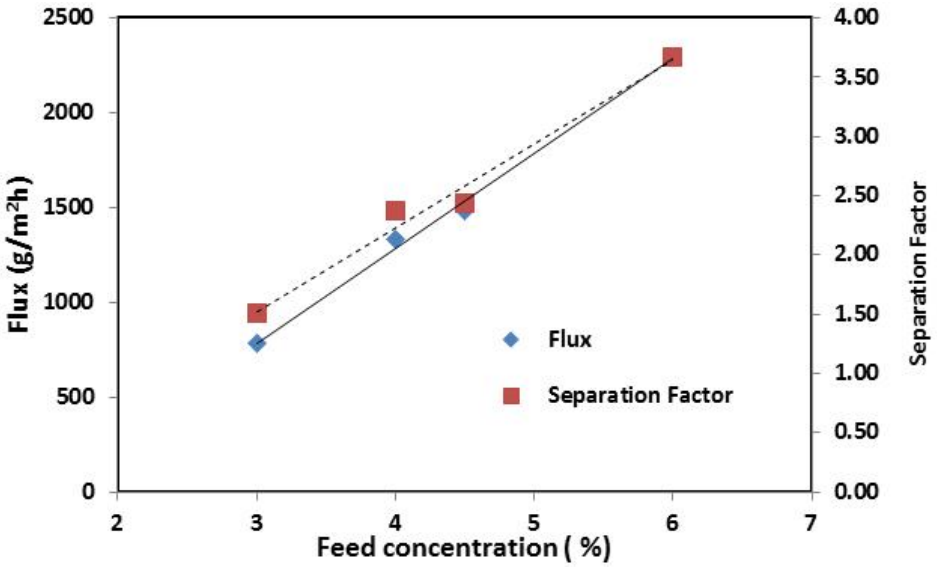

Figure-3. Flux and separation factor as a function of ethanol feed concentration on a PDMS membrane at 45ºC.

The separation factor reached 3.67 at the highest flux of about 2300 $g/m^2/h$ at the 6% ethanol concentration. Conditions adopted are optimized for maximizing the flux while obtaining acceptable separation factor.

Ethanol dehydration via optimized silica membrane

Variation of flux with time during dehydration on optimized silica membrane at 65ºC is depicted in Figure-4 at ethanol feed concentration of 95% .This trend is in accordance with that reported by Khan *et al* (2015) using the same type of membrane (Khan J. R. *et al*., 2015). The relatively high flux is attributed to the high applied pressure and also the high vacuum which have been adopted to increase flux while obtaining an acceptable separation factor of about 122.

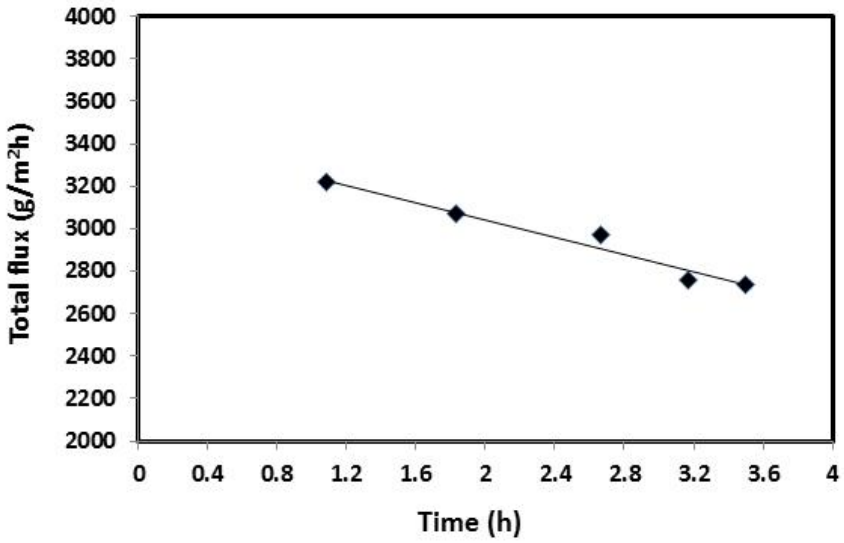

Figure-4. Variation of flux with time during dehydration on optimized silica membrane at 65 ºC and ethanol feed concentration of 95%.

CONCLUSIONS

Based on preliminary investigations, it is concluded that pervaporation proves to be a viable option for separation and dehydration of ethanol due to its technical performance and minimum energy usage. The conditions have been optimized to obtain higher flux at acceptable separation factors for both the concentration and the dehydration modes. PDMS flux ($g/m^2/h$) varied between 780 and 2300 with a maximum separation factor of 3.67. Moreover, at about 95% initial ethanol concentration, the hydrophilic drying membrane flux ranged between 2700 and 3400 ($g/m^2/h$) and the separation factor reached about 122. Investigations on actual fermentation broth, integrated dehydration scheme and process optimization are recommended. Further, endeavors for improvement of hydrophobic and hydrophilic membrane characteristics are mandatory.

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