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Potential of large-scale application of pervaporation for bioethanol production from rice straw

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ABSTRACT

Pervaporation is a promising technique for recovery of volatile compounds from aqueous solutions. Due to technical and economic considerations, its application on large scale for bioethanol production from rice straw is limited. In this article, aqueous alcohol solution produced from pretreated rice straw through sequential saccharification/fermentation using Novozymes Cellic® CTec3 and *Saccharomyces cerevisiae*, respectively was subjected to the pervaporation technique. Experiments were conducted on semi-pilot scale set-up using hydrophobic polydimethylsiloxane spiral wound membrane. The fermentation broth with ethanol concentration of 3% and 7.5% (w/w) was subjected to pervaporation at different temperatures and time intervals, after pretreatment to remove suspended matters and pH adjustment. The process performance in terms of flux and separation factor was analyzed. Further, a techno-economic study for the pervaporation application for a commercial scale capacity plant is presented to illustrate the preliminary economics of its application. Finally, recommendations for improving the process economics are also suggested.

Keywords: Bioethanol; Economics; Fermentation; Pervaporation; Recovery

1. Introduction

Production of bioethanol as a green fuel is the focus of numerous R&D institutions [1,2]. Agricultural residues including rice straw, cotton stalks and food industry residues are subjected to pretreatment, saccharification (using enzyme to produce fermentable sugars), fermentation and separation of bioethanol from the fermentation broth [3,4]. Conventionally distillation process is used to achieve the required separation of alcohol from water [5,6]. The main limitation of this approach is the intensive energy consumption and technical problems such as formation of azeotrope [7]. With the recent advances in membrane separation technology, pervaporation (PV) has emerged as a novel process for separating volatile compounds from liquid streams. This technology is highly flexible and reflects minimum footprint and energy consumption as compared to distillation [8]. Numerous membrane materials are used including polysulfone (PS), polyethersulfone (PES), polydimethylsiloxane (PDMS), polyvinyl alcohol (PVA), etc. [9]. So, basically, two membrane arrangements could be used. The first is hydrophobic membrane for bioethanol concentration while the second-one adopts hydrophilic membrane for bioethanol dehydration. For advanced PV scheme, conventional distillation is interposed between the two membrane types [10]. Thus, adopted schemes may comprise both conventional and membrane modules. Typical reported separation factor for those membranes (in case of alcohol separation) is in the range of: "1–31"for polydimethylsiloxane (PDMS),"8–26"

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for poly(1-trimethylsilyl-1-propyne) (PTMSP), "4–8.3" for polyoctylmethyl siloxane (POMS), 45.6 for styrene-g-fluoroalkyl acrylate copolymer/PDMS,"5.2–120" for zeolites MFI and silicalite [1]. In this paper, some technical aspects of ethanol recovery from fermentation broth are investigated on semi-pilot plant level. Furthermore, a conceptual case study is presented to illustrate the technical and cost indicators for application of hybrid PV/distillation system.

2. Recovery of bioethanol from fermentation broth using PV semi-pilot system

2.1. Materials

Aqueous alcohol solution produced from pretreated rice straw through sequential saccharification/fermentation using Novozymes Cellic® CTec3 and *Saccharomyces cerevisiae* was used in this study. Fresh ethanol (95%) (ADWIC) was used to enrich the fermentation broth to reach ethanol concentration of 3% and 7.5% (w/w) (ethanol concentration was determined using HPLC) and sodium hydroxide was used for pH adjustment.

The hydrophobic/organophilic module mounted in this set-up is a spiral wound PDMS of effective area 0.6 m^2 which has been supplied by Pervatech.

2.2. Methods

A semi-pilot plant experimental pervaporation set-up has been operated, as previously described by the authors [11]. The fermentation broth was filtered, pH adjusted to 4.5 using sodium hydroxide and enriched with ethanol (ADWIC) to reach ethanol concentrations of 3% and 7.5% (w/w). Briefly, the filtered solution is fed to 10 L jacketed stainless steel tank with a temperature-controlled circulating water bath (Polyscience). The heated solution is transferred by a centrifugal pump (Lowara) to the PDMS membrane module for increasing the ethanol concentration. The output is cooled through two sequential stainless steel 316 tubular condensers of total cooling area 0.25 m^2 connected to a vacuum pump (MTI Corp.) operating below 0.1 mbar. Condensers are cooled using a chiller at a temperature of about 4–7°C.

The system is first flushed at the desired temperature for 15 min using a dilute water ethanol solution. Then, the system is run for different time intervals at the desired flow rate (about 1 m^3/h) and temperature 30°C–55°C, applied pressure 1 bar and vacuum below 0.1 mbar to reach steady state. Samples of the permeate are collected at specific time intervals, and the ethanol concentration was determined using a digital refractometer (CETI).

Flux and separation factor have been determined for performance assessment according to the following equations:

$$J = \frac{Q}{A} \tag{1}$$

where J is the flux (g/m^2 h), Q is the collected permeate weight in an hour (g/h), A is the membrane area (m^2).

$$\alpha = \frac{\left(Y_w / Y_e\right)}{\left(X_w / X_e\right)} \tag{2}$$

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.

Technical aspects of the proposed system for hybrid pervaporation/distillation system for a typical capacity of 1,000 m^3/d of fermentation broth are presented. These include process description, basic system design, material balance, and equipment specifications. Economic aspects and cost indicators were estimated based on up-dated cost data.

3. Results of ethanol recovery by pervaporation

3.1. Effect of initial ethanol concentration

Fig. 1 depicts the change of flux and separation factor at the initial steps of operations at temperature about 40°C. It is clear from Fig. 1a that for 3% (w/w) ethanol concentrations the initial flux is high, which may be attributed to accumulation of water vapor and rapid condensation in that stage. This point of view is supported by the lower initial values of the separation factors. Steady state conditions are almost obtained after 40 min of operation. The attained separation factor after 40 min is shown in Fig. 1a and b were about 1.8 and 2.2 for 3% and 7.5% (w/w) ethanol concentration, respectively. The flux value is 760 and 600 g/m^2 h for 3% and 7.5% (w/w) feed concentration, respectively. Decrease of flux at high initial ethanol concentrations

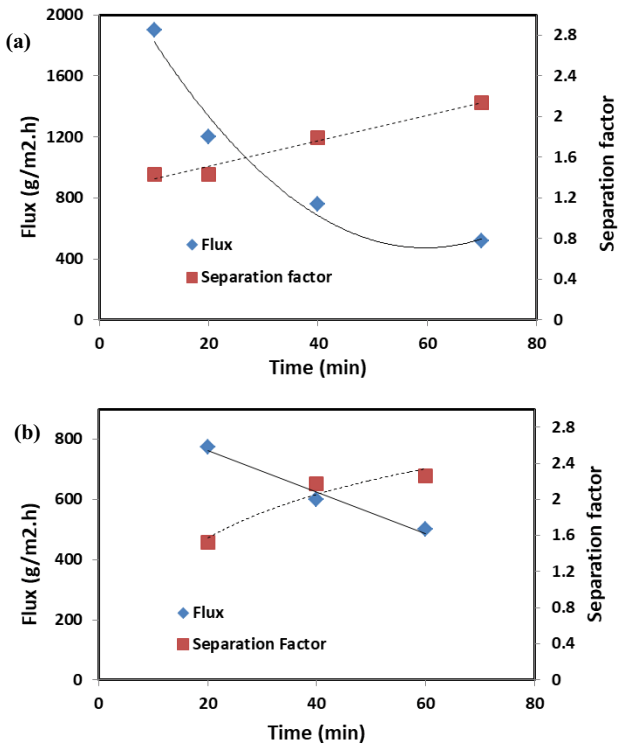

Fig. 1. Time dependence of flux and separation factor at (a) 3% and (b) 7.5% initial ethanol concentration.

may be attributed to higher ethanol evolution in the second case. It is worth mentioning that the permeate ethanol concentration are 6.5% and 15.5% for 3% and 7.5% (w/w) feed concentrations, respectively.

3.2. Temperature effect

Fig. 2 illustrates the effect of temperature on both flux and separation factors. It is observed that both flux and separation factor values increase as the temperature increases. It is noted that there is no significant change in flux between 40°C and 44°C. This may be attributed to insignificant difference in vapor pressure of ethanol and water at the prevailing operating conditions [12].

Separation factor values were almost constant (about 2.1) for temperature range of 44°C–53°C. On the contrary, the flux values increased from 617 to 1,277 g/m² h in the same temperature range.

The findings of the experimental work showed higher values than Mori et al. and Moermans et al. [13] who used PDMS membrane at temperature of 66°C and 50°C recording flux valued of 150 and 100 g/m² h, respectively. On the other hand, comparable values (1170 g/m² h) were obtained by Liu et al. [14] and higher flux values (1,493 g/m² h) were obtained by Liu et al. [15] who worked on pilot scale using PDMS-based membranes at 60°C. This variation may be attributed to difference in the applied process conditions from that applied in this study.

It is worth mentioning that rather similar work was conducted by the authors using synthetic 6% ethanol solution and reached 3.7 separation factor and flux of about 2,300 g/m² h at 45°C [11]. The current lower results may be attributed to using real fermentation broth which affects the separation performance of the membrane.

The proposed system comprises a hybrid pervaporation/distillation system for concentration and dehydration of bioethanol. Technical and economic aspects are presented below.

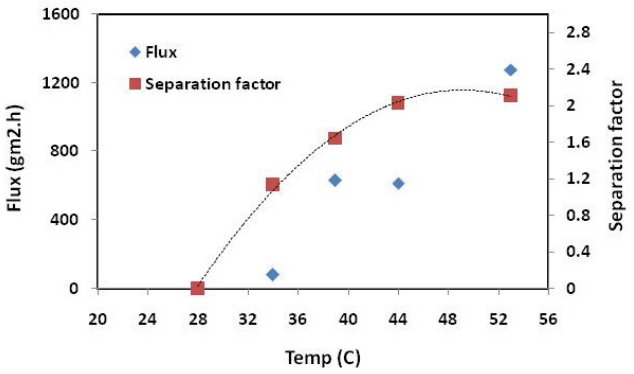

Fig. 2. Temperature effect on flux and separation factor at 7.5% ethanol initial concentration.

4. Technical and economic indicators for industrial scale hybrid pervaporation/distillation process for bioethanol recovery from 1000 ton/d fermentation broth

The objective of this section is to illustrate the techno-economic aspects of pervaporation application in bioethanol production. To identify the potential of applying pervaporation in bioethanol production from agricultural waste, a system comprising hybrid pervaporation/distillation is proposed. Both technical and economic indicators are presented for a plant capacity 1,000 t/d of pretreated fermentation broth.

4.1. Technical indicators

The process flow diagram of the adopted system is shown in Fig. 3.

The system comprises three main units as follows:

- Hydrophobic pervaporation membrane unit (PV1) or ethanol concentration unit to increase the low ethanol

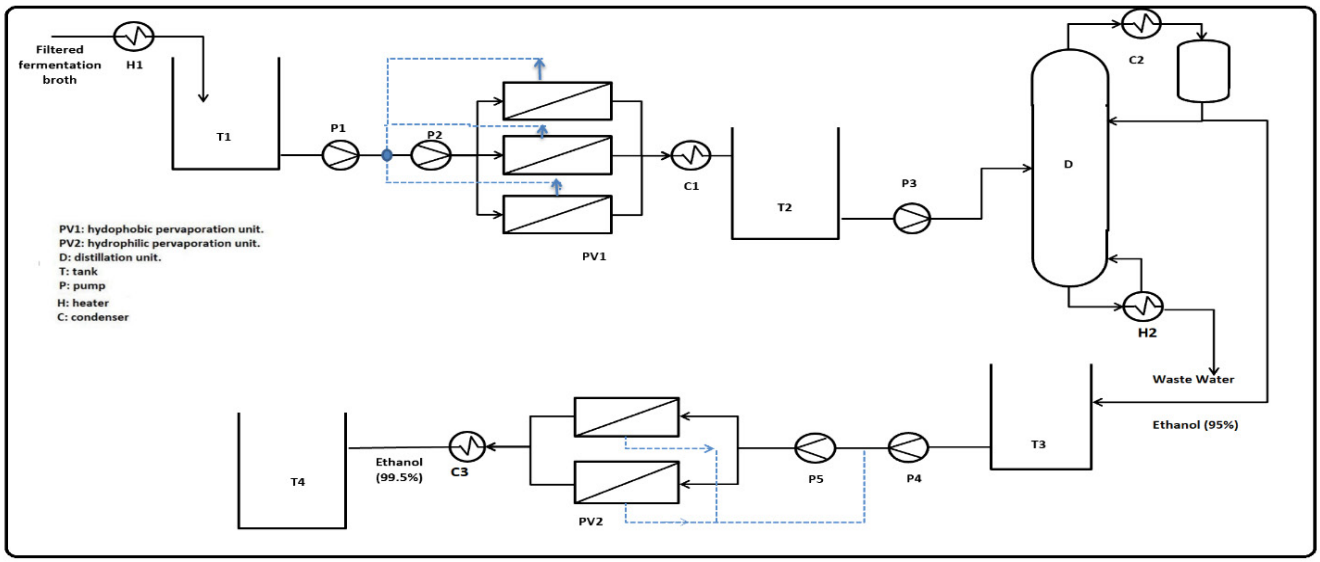

Fig. 3. Flow diagram of proposed hybrid pervaporation/distillation process for bioethanol recovery from fermentation broth.

concentration produced from the fermentation broth of pretreated rice straw (3%) to a practically accepted feed concentration for distillation 15%–20%.
- Distillation unit (*D*) using conventional distillation system to reach near azeotropic concentration (95%).
- Hydrophilic pervaporation membrane (PV2: for ethanol dehydration) to reach ethanol concentration of about 99.5%. The material balance of the proposed industrial scale process for concentration and dehydration of bioethanol is illustrated in Fig. 4.

The main technical process features and the specifications of the major equipment of the system are presented in Table 1.

4.2. Cost indicators

The equipment cost is based on published cost data updated using CE equipment/index. Further, basis for cost item determination is presented in the cost estimate Tables 2 and 3 [1,9,10].

Table 2 shows the breakdown of capital cost for bioethanol recovery from 1,000 m^3/d fermentation broth.

As shown in Table 2 the obtained capital cost of the unit amounts to about $5.27 million.

The estimated annual cost and cost/ton of ethanol product are illustrated in Table 3.

Table 3 depicts annual operating cost estimates which amount to $1.626 million. The total annual cost is $1.98 million. The cost per ton ethanol is $226.5/ton. The total production cost per liter of ethanol is about $0.181.

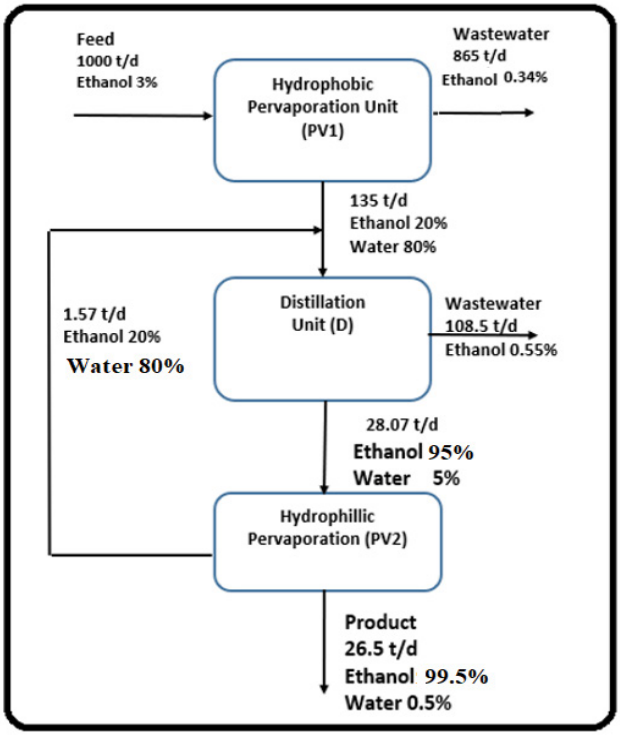

Fig. 4. Material balance for the proposed industrial scale bioethanol recovery hybrid pervaporation/distillation system from 1,000 ton/d fermentation broth.

Table 1
The main process features and equipment specifications for the proposed hybrid pervaporation/distillation system for 1,000 t/d fermentation broth

Unit	Specifications
Hydrophobic PV1 membrane unit	- Membrane: Hydrophobic, polymeric spiral wound, with area 4,687.5 m^2, α = 4, flux 1.9 L/m^2 h. - Feed tank: SS 316, 50 m^3. - Feed heater: 200 m^2. - Feed pump: centrifugal SS 316, 50 m^3/h, 50 m head. - Circulating pump: SS 316, 250 m^3/h, 50 m head. - Vacuum pump(s): 1.5 m^3/s, 0.1 bar (a). - Auxiliaries, instrumentation and electrical.
Distillation unit	- Distillation column: SS 316 (1 m diameter, bubble caps trays (16 tray) with reflux). - Condensers: (200 m^2). - Reboiler: (200 m^2), SS 316. - Feed tank: SS 316, 20 m^3. - Feed pump: (centrifugal SS 316, 10 m^3/h, 20 m head). - Reflux tank: SS 316. - Auxiliaries, instrumentation, electrical.
Hydrophilic PV2 membrane unit	- Membrane: hydrophilic, tubular, with area 600 m^2, α = 800, flux 2 L/m^2 h. - Feed pump: centrifugal SS 316, 2 m^3/h, 50 m head. - Circulating pump: SS 316, 20 m^3/h, 50 m head. - Vacuum pump(s): 0.5 m^3/s, 0.1 bar (a). - Feed tank: SS 316, 20 m^3. - Feed heater: 100 m^2 - Product tank: SS 316, 50 m^3. - Auxiliaries, instrumentation and electrical.

Table 2
Estimated capital cost for the proposed hybrid pervaporation/distillation system (for 1,000 m^3/d fermentation broth)

Item	Cost ($1,000)
1. Equipment	
A. Pervaporation unit (PV1) including: Hydrophobic membranes ($250/$m^2$), heater, condenser, feed and vacuum pumps, tanks electrical and instrumentation and auxiliaries.	1,497
B. Distillation unit (*D*): including distillation column, reboiler, condenser, pumps, tanks, electrical and instrumentation, and auxiliaries.	675
C. Pervaporation unit (PV2) including: hydrophilic membranes ($40/$m^2$), heater, condenser, feed and vacuum pumps, tanks, electrical and instrumentation and auxiliaries.	445
Total equipment cost (EC)	2,617
2. Installation (20% of EC)	523.4
3. Piping (20% of EC)	564
4. Electrical and instrumentation (15% of EC)	392.6
Total direct cost (DC)	4,056.4
5. Other costs (engineering, contingency, etc. 30% of DC)	1,216.9
Total capital cost	5,273.3

Table 3
Estimated annual cost and cost/ton of ethanol product

Item	Basis	Annual cost ($1,000/Y)
1. Membrane's replacement	15% replacement/Y $400/$m^2$	211.8
2. Utilities		
- Electricity	900,000 kWh/Y ($0.07/kWh)	90
- Steam	52,000 t/y ($20/t)	1,040
- Water	330,000 m^3/y ($0.1 m^3)	33
Total utilities		1,136
3. Maintenance	3% of direct capital cost	158.2
4. Labor	120 man monthly/Y "average" ($1,000/man month)	120
Total O&M		1,626
II. Amortization	Plant life 20 Y, interest rate 3%	354.5
III. Total annual cost		1,980.5
IV. Cost/ton	Annual production = 26.5 T/d × 330 d/Y	226.5

The present case is considered an optimistic scenario. Two other scenarios were considered.

Conservative scenario (both capital and operating cost increased by 15% of the basic case and ethanol production is 90% of the basic case.

Pessimistic scenario (both capital and operating costs increase by 30% of the basic case and ethanol production is 80% of the basic case.

The cost/l of pure ethanol is estimated to be $0.181, 0.232, and 0.295/L for optimistic, conservative and pessimistic scenarios, respectively.

It is worth mentioning that the present study is based on currently applied membranes on commercial scale. However, there are growing research endeavors to produce membranes with higher selectivity and flux values as reported by Peng et al. [1]. Further, operating conditions regarding solution flow rate and pressure should be optimized.

The competitive advantage of pervaporation has been reported in Zentou et al. [16]. Techniques including distillation, pervaporation and vacuum fermentation costs were compared and costs per liter of alcohol were reported as $1.3, $0.8 and $0.6/L, respectively [16].

5. Conclusions

Pervaporation currently applied for many solvent recovery systems and dehydration could have a potential role in bioethanol production from residual agricultural wastes. Experimental evidence for success of pervaporation applicability in the process of ethanol recovery and increasing the concentration from fermentation broth of pretreated rice straw is validated under moderate operating conditions in this study. Potential of pervaporation technology application in bioethanol production is illustrated through proposed hybrid pervaporation/distillation system.

The Case study presented for 1,000 t/d (3% ethanol) fermentation broth, showed that cost of ethanol (99.5%) range is "$0.181–0.295/L".

Further work is recommended to optimize PV performance. Development of PV membranes to improve performance and reduce its cost is mandatory for large scale application of PV in bioethanol industry.

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