

DEHYDRATION OF INDUSTRIAL ETHANOL BY PERVAPORATION

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ABSTRACT

Pervaporation (PV) is an advanced membrane separation technique used for the separation of constant boiling mixtures or Azeotrope. In the purification of ethanol from ethanol/water mixture by distillation, a maximum concentration of 95% by mass can be achieved. At this concentration level, the mixture forms an azeotrope and allows no further enrichment by simple distillation. PV technique has been used for the production of absolute alcohol from industrial alcohol. Experimental work has been done and successful enrichment of industrial alcohol has been achieved operating at normal operating conditions (70 °C and 2.0 bar) using designed PV rig and characterized by Gas Chromatograph (GC).

Keywords: *Azeotrope, Ethanol/Water Separation, Membrane Separation Technique, Pervaporation*

INTRODUCTION

Pervaporation is an energy intensive process and also gives high purity product by which absolute alcohol can be effectively produced from industrial alcohol (Zhu et al., 2010). Ethyl alcohol is manufactured by fermentation of molasses in a mash column. Concentration of this alcohol is then enriched by distillation process using rectification column. When concentration of alcohol water mixture reaches 95%, composition of vapor and liquid phase becomes equal; forming an azeotrope (Baker, 2007). Thus no further enrichment of ethyl alcohol is possible by straight forward distillation; as components of the azeotropic mixtures have very close boiling points (Backhurst et al., 2002). Absolute alcohol has increasing demand at present age as it is blended with gasoline to manufacture Gasohol and also used as direct fuel (power alcohol). In

order to increase the concentration of ethyl alcohol from 95%, many conventional techniques are in practice including Liquid-Liquid Extraction, Extractive distillation, Azeotropic distillation, and Adsorption etc. All these techniques consume high amount of energy, require external extracting chemicals and downstream processing. So instead of using these conventional techniques, an advanced green separation technique "Pervaporation" is employed (Usman et al., 2009). It is a membrane separation technique (Nunes and Peinemann, 2006, Yeh et al., 2012). It is capable of breaking azeotropes, handling heat sensitive and less volatile materials and treating organic separations from industrial wastes (Yuan et al., 2011, Meireles et al., 2013). Along with energy intensive separation method, this technique is useful for protecting environment from pollution, global warming and operating hazards with a minimal production cost and ultrafine quality product (Afonso and Crespo, 2005).

Pervaporation process due to its flexibility in operation, in-line nature and simple process schematics, is being used in many of industries for diverse separation methods. Name of this membrane-based process is derived from the two basic steps. Firstly the permeation through the membrane and then its evaporation into the vapor phase. Membrane of Pervaporation module acts as a discerning obstacle among feed constituents does not allow passing out the specific particles or group of particles when consider the action of a driving force. The major driving forces causing transport through the membrane are difference in transport rate, chemical potential difference and partial pressure difference of the feed components. Selection of membrane and membrane module designing is the core issue in Pervaporation unit. Membrane serves as a discriminating obstacle between two phases and causes separation by remaining impermeable to specific particles when consider the action of a driving force (Nunes and Peinemann, 2006; Braisher et al., 2006). Schematic diagram of ethanol dehydration by Pervaporation Process is shown in Fig 1 (Nguyen et al., 2008).

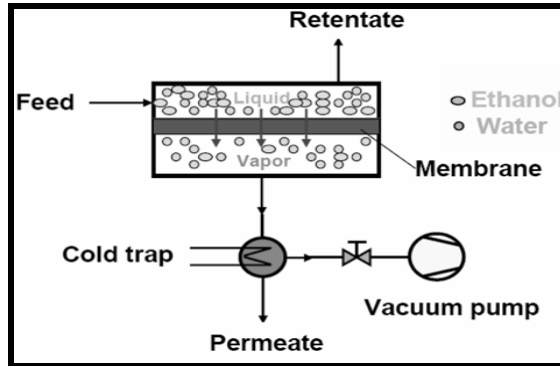
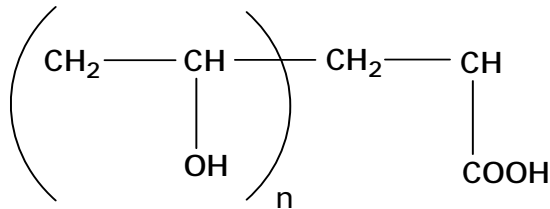


Fig 1: Schematic Diagram of Ethanol Dehydration by Pervaporation Process (Nguyen et al., 2008)

There are several types of synthetic polymeric composite membranes, but PVA (Polyvinyl Alcohol) membranes have proven best results for the ethanol-water separation (Burshe et al., 1997). It is a hydrophilic, nonporous dense membrane having structure (Braisher et al., 2006; Yampolskii and Pinnav, 2006).



Equipment containing the selective membrane is termed as the membrane module (Nunes and Peinemann, 2003). Membrane module can be of tubular, hollow fiber, spiral wound or plate and frame type. Quantitative comparison has been reported in the favor of the latter one (Bahara, 1998). The feed constituent which passes through the membrane is termed as permeate and the remainder of the feed stream which retains on the membrane is termed as retentate. Transport through the membrane is followed by a three step mechanism called Solution-Diffusion Model which involves sorption, diffusion and desorption (Baker, 2007; Perry and Green, 2008). Design of Pervaporation membrane module and operational conditions are the responsible factors for process. It is a proven fact that 10 °C increases in feed temperature increases the separation by 20-40 %. However increase in feed side pressure has only a minute effect on separation efficiency (McCabe et al., 2004).

A number of studies have been developed for the separation of ethanol-water separation via pervaporation. All these studies emphasize on efficient dehydration of ethanol at ambient conditions. Chen et al. presented the interesting studies covering the determination of permeation flux and separation factor of water/ethanol system by using PVA membrane (Chen et al., 2010). Sunitha et al used the cross linked chitosan membrane and varied the different factors e.g. membrane thickness, permeate pressure and feed composition to identify the optimum conditions (Sunitha et al., 2012). Also, increase in permeation flux was achieved by raising the temperature upto 70 °C and by decreasing the membrane thickness upto 200µm by Pakkethati and his co researchers (Pakkethati et al., 2011). Present work involves the separation of water ethanol mixture by means of PVA membranes using plate and frame membrane module via pervaporation technique.

Experimental

Materials

Commercial grade ethanol was obtained from local market and used without any pretreatment. 95% ethanol solution was prepared using distilled water. PVA membrane is also purchased from local market.

Experimental

Pilot-Plant used for experimental work has a capacity of 5000 cm³ was designed and locally fabricated and is shown in fig 2.



Fig 2: Pervaporation Experimental Rig

Flow diagram of experimental rig is shown in fig 3.

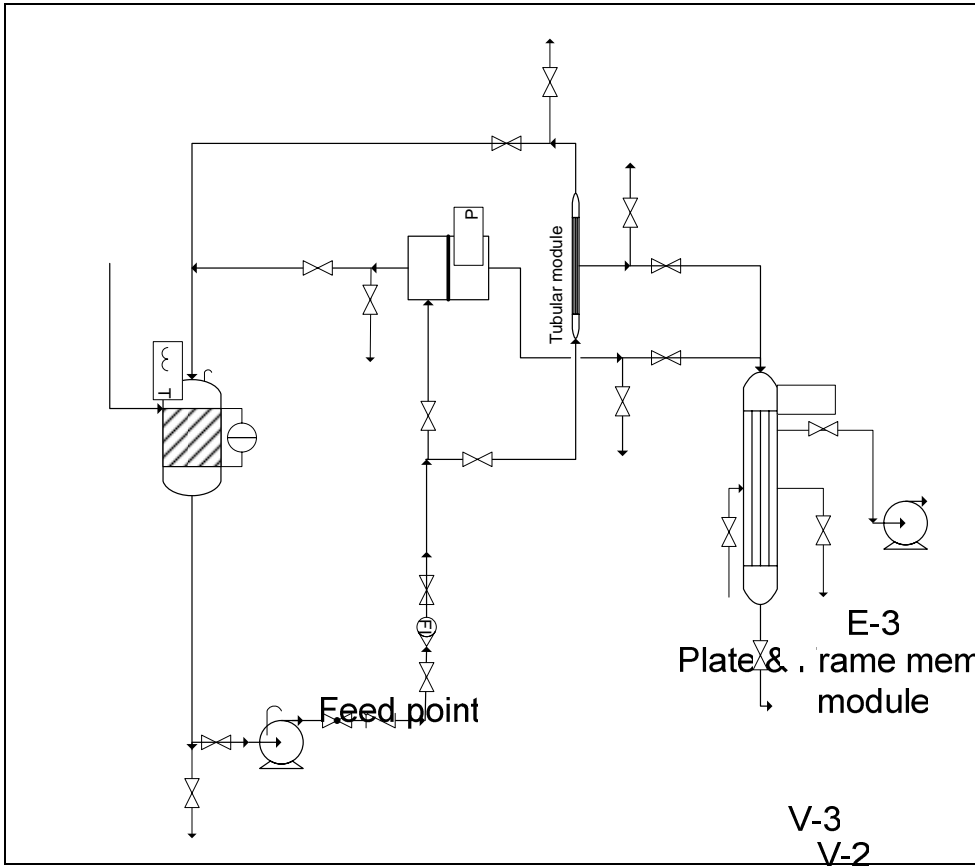


Fig 3: Flow Sheet of Diagram of Designed Pervaporation Rig

Pervaporation unit is equipped with feed tank with electric heating arrangement, magnetic drive circulation pump, plate and frame type membrane module, tubular module, condenser (plate and frame type), dosing pump, vacuum pump, temperature, pressure and flow controllers. Room temperature at the time of experiment was noted to be 32 °C. Azeotrope of 95% ethanol and 5% distilled water (4000 ml on 98% Basis; EtOH = 3878 ml, Water = 122 ml) was preheated via controlled electric heating system upto 70 °C. Heated feed stream was fed into the plate and frame type Pervaporation module at 70 °C and 2.0 bar pressure and feed flow rate of 0.2 g/m using circulation pump. Vacuum of -0.2 bar was applied at the downstream side to increase the membrane flux rate. Effective surface area of the membrane used was 0.0102 m². The flux of

I-1 Rotameter

V-15

V-10

Vent

Sampl

P-5

I-3 Pressure

E-3 Plate & frame membrane module

V-3

V-2

Feed point

Vent

P-29

I-2 Temperature indicator

E-5

Feed heating tank

P-1

P-24

V-17

P-20

V-20

P

4

water through membrane can be calculated using equation (i) (Braisher et al., 2006).

$$J_i = Q_i / A \times t \dots\dots\dots(i)$$

Where

Q_i = Moles of component 'i' permeated in time 't'

J_i = Flux of component 'i' (Kg/ hr.m²)

A = Surface area of membrane which is effected (m²)

Liquid feed mixture associates one side (upstream side) of the membrane and water is removed as a vapor from the other side.

Samples of retentate and permeate were collected after each hour and marked with collection time. Volume of permeate was noted after each one hour and cumulative volume was calculated. Permeate concentration was checked using Gas Chromatograph CP (GC) 3800 Varian, Germany. Chromatogram for 96.226% is shown in fig 4.

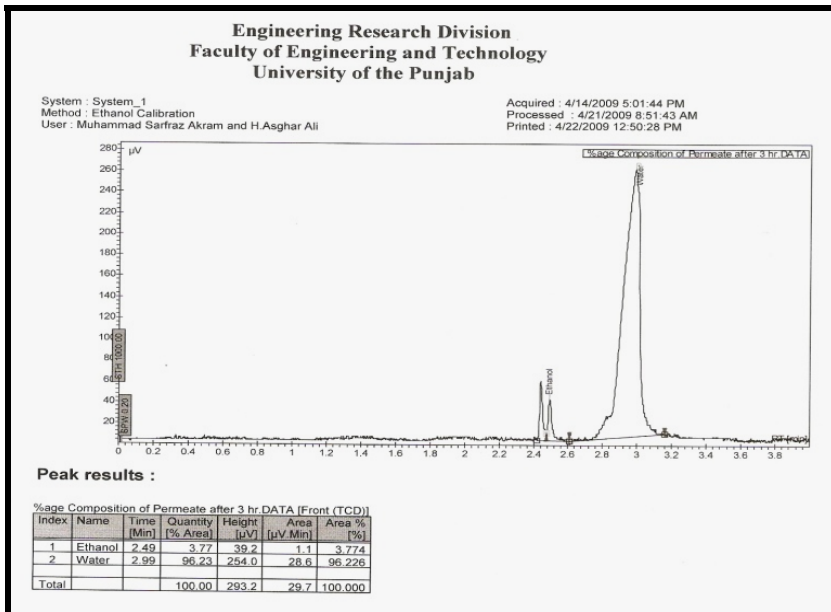


Fig 4: Chromatograph for 96.62 % Alcohol recovery by Pervoaporation

Azeotrope was broken & the concentration of ethanol mixture was successfully enriched upto 96.62 %. Calculations based on experimental observations have been presented in Table 1:

Table 1: Observations and Calculations for Experiment Performed on PV Experimental Rig

No. of Obs.	Time Elapsed (hr)	Permeate (Water)		Membrane Flux Rate* (Kg/m ² .hr)	Concentration of Retentate** (Alcohol) (%)
		Volume Collected after each hr (ml)	Cumulative Volume Collected (ml)		
1.	1	8.6	8.6	0.802	95.204
2.	2	8.4	17.0	0.784	95.405
3.	3	8	25.0	0.747	95.597
4.	4	7.7	32.7	0.719	95.783
5.	5	7.4	40.1	0.690	95.962
6.	6	7.2	47.3	0.672	96.137
7.	7	6.9	54.2	0.644	96.305
8.	8	6.7	60.9	0.625	96.468
9.	9	6.3	67.2	0.588	96.622

*Flux calculated by equation (i)

** Concentrations are determined by GC

RESULTS AND DISCUSSION

It is clear from the collected data and graphical results that Pervaporation technique successfully broken the azeotropic mixture of ethanol water and raised concentration up to 96.62 %. Volume of permeate decreased as the time elapsed thus showing a decrease in water concentration in feed mixture, increasing alcohol concentration in retentate. Increase in cumulative volume of permeate showed continue separation of alcohol water mixture resulting in increase in permeate volume. Flux rate of water molecules also decreases continuously as the time elapsed.

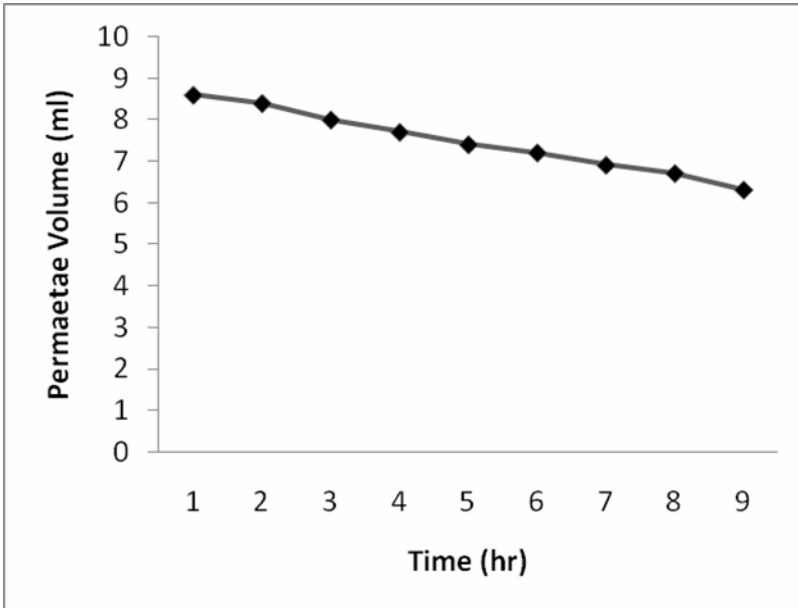


Fig 5: Permeate Volume Collected after each hour versus Time Elapsed

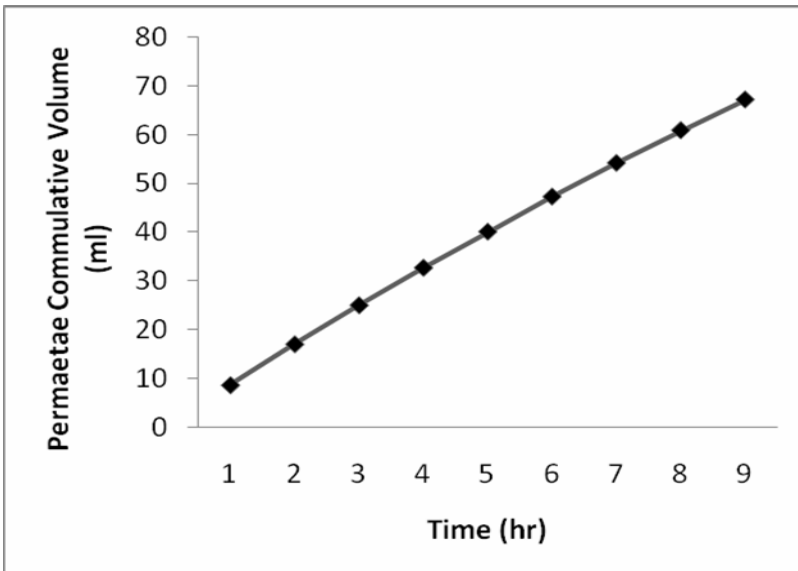


Fig 6: Cumulative Permeate Volume Collected after each hour versus Time Elapsed

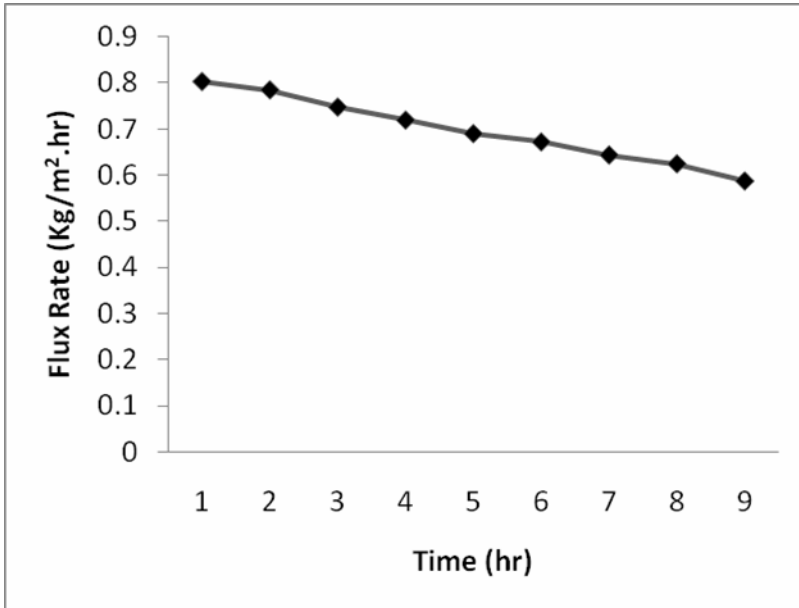


Fig 7: Membrane Flux Rate versus Time Elapsed

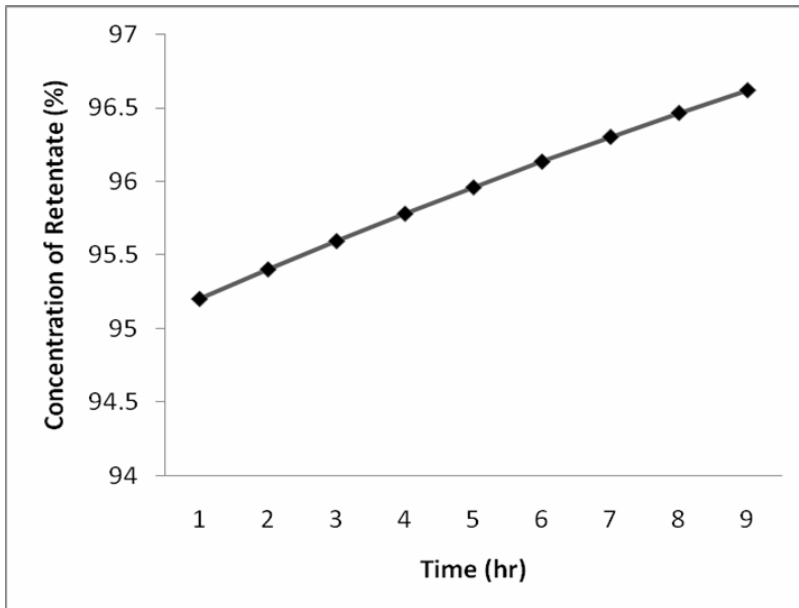


Fig 8: Retentate Concentration versus Time Elapsed

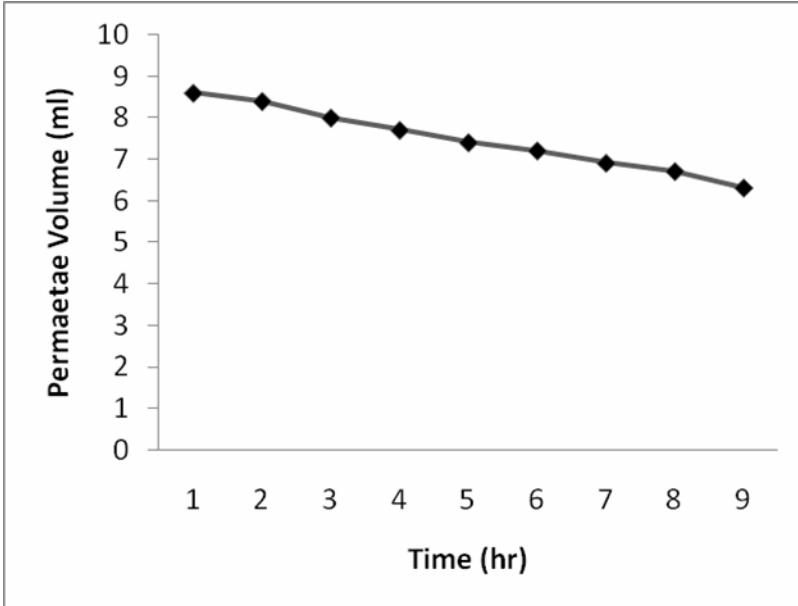


Fig 9: Permeate Volume Collected after each hour versus Time Elapsed

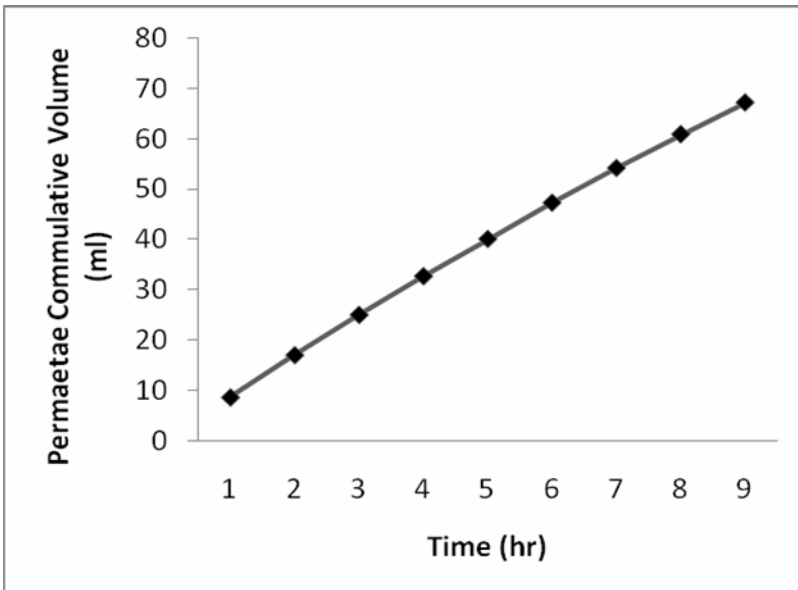


Fig 10: Cumulative Permeate Volume Collected after each hour versus Time Elapsed

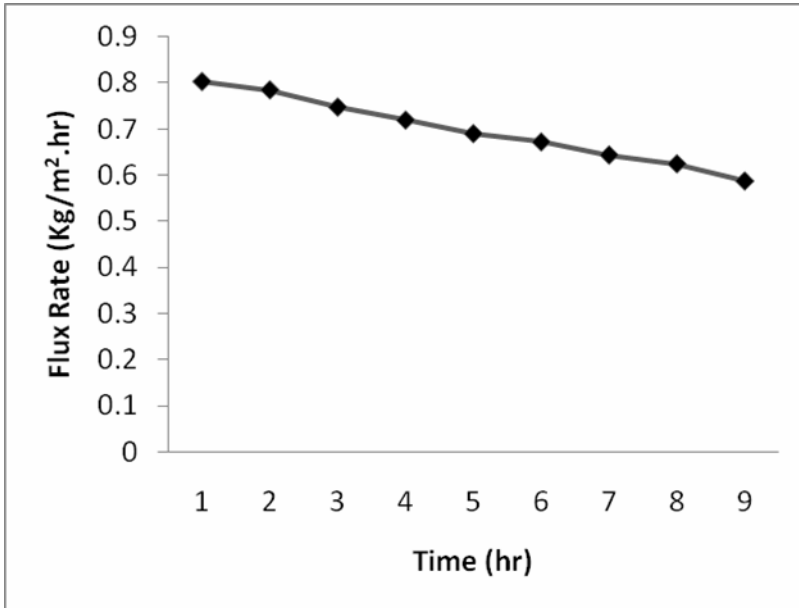


Fig 11: Membrane Flux Rate versus Time Elapsed

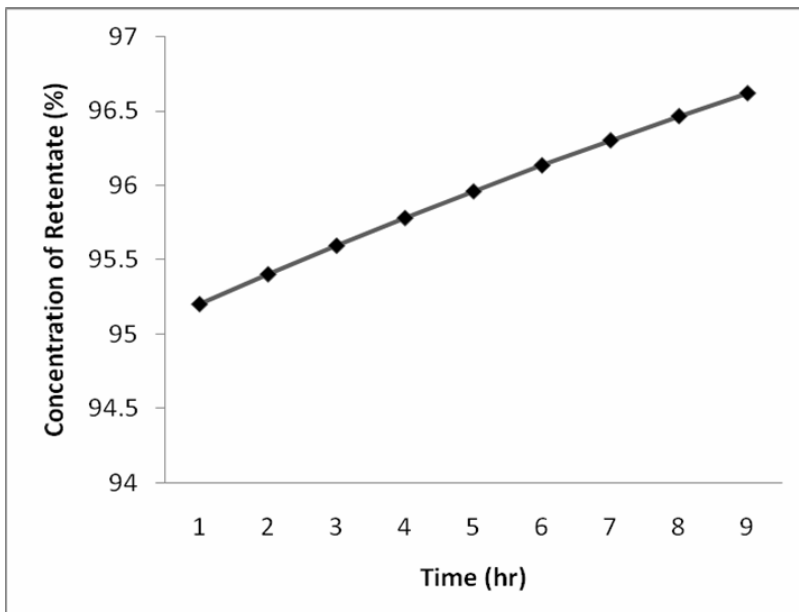


Fig 12: Retentate Concentration versus Time Elapsed

CONCLUSIONS

Pervaporation method successfully break EtOH-H₂O azeotrope raising concentration from 95.0 % to 96.62 % using experimental pervaporation rig utilizing plate and frame membrane module. Pervaporation technique proved itself capable for separating mixtures that present hurdles in their separation (like azeotrope, constant boiling mixtures, heat sensitive mixtures, nonvolatile and mixtures with relative volatility \approx 1). 96.62 % Ethanol at 60 °C temperature was obtained as a retentate. Permeate, in vapor form, was condensed in a condenser and recycled if necessary. Concluding, 96.62 % ethanol has been produced using low grade energy, economical and safer operational mode without using any external chemical or downstream processing. Although the flux rate for the experimental rig is low due to smaller contact area, however this rate can be increased by performing the separation on industrial scale setup. Pervaporation separation can be made further efficient by using highly selective membrane for each particular azeotrope.

FUTURE RECOMMENDATIONS

Pervaporation technique has proven itself a successful separation technique and being applied all over the world. Some of the leading perspectives of Pervaporation separation technique are separation of azeotropic mixtures in chemical process industries, organic-organic separation, separation of dissolved organics from water, increasing distillation column efficiency by hybrid Pervaporation unit, Increasing reaction yield by perstillation (Baker, 2007; Afonso and Crespo, 2005). There is prime requirement to make developments in the area of manufacture of membranes using the latest polymeric materials that are much more specific in their selectivity, ability to deal with many close boiling mixtures or azeotrope in diversified fields to enhance separation efficiency, operating capability at sever operational conditions and make their service life longer.

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