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### **Energy Efficient Hybrid Pervaporation / Distillation Process for Ethanol - Water Separation**

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#### **ABSTRACT**

Increasing energy demand in the chemical process industry is one of the major factors for the development of alternative separation processes to conventional separation processes. Compared to conventional distillation, hybrid separation combining two or more unit operations may work out to be energetically and economically more efficient in separations involving close boiling or azeotropic composition. In this paper we demonstrate this using ethanol-water as the model system and separation by Distillation -Pervaporation (D + PV) hybrid unit. Compared with azeotropic distillation, pervaporation is more energy efficient when the feed ethanol concentration is high. 80 % energy saving is possible using PV. At low feed ethanol concentrations, D + PV is more attractive compared to only PV. 40 % energy can be saved as compared to PV. A method for the selection of the number of trays of the distillation column is also discussed in this paper.

**KEYWORDS:** Pervaporation, Hybrid Separation, Membrane, Azeotropic distillation, Vapor permeation

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## INTRODUCTION

Distillation is a popular separation technology conventionally used for the separation of liquid mixtures. One of the major drawbacks of conventional distillation is that, it is difficult to separate the azeotropic or constant boiling mixtures. Pervaporation is one of the most promising membrane technologies offering solution to dehydration of organic compounds, recovery of organic compounds from aqueous solutions, separation of organic mixtures etc <sup>1</sup>. Solution diffusion model is considered to be more suitable for describing transport through dense pervaporation membranes <sup>2</sup> Combined process consisting of distillation and pervaporation/vapor permeation offers economically attractive alternatives as they can simplify the process structure, reduce the energy consumption and avoid the entailers for the separation of azeotropes and close boiling solutions<sup>4,5,6</sup>. The simulation of an existing plant revealed that 12% saving in the total annual cost could be achieved by using 32% additional membrane surface <sup>8</sup>.

In this paper we present Energy Efficient Hybrid Pervaporation / Distillation Process for Ethanol - Water Separation. McCabe-Thiele method has been used for distillation tray calculations while Rautenbach model based on solution diffusion theory has been used for pervaporation calculations.

## Model Development

### *Distillation model*

A distillation unit comprising of column, total condenser and partial reboiler was considered for the study. The model uses mass and energy balances at each tray, coupled with vapor liquid equilibrium data. UNIQUAC and Virial equations of state have been used to generate the vapor liquid equilibrium (VLE) of the mixture.

### *Pervaporation model*

Among the diverse pervaporation models described in literature, the solution diffusion model provides an accurate description of the behavior of membranes and the dependence of membrane transport on pressure, concentration etc. and hence is widely used <sup>9</sup>.

Composite membranes are used in the process and consist of a thin selective layer placed above a porous supporting layer which gives mechanical stability to the membrane. The permeation of the component through this porous layer is driven by diffusive or pore flow. The pressure through the membrane material is assumed to be constant so that the driving force chemical potential gradient gets simplified to concentration gradient. In the present study Rautenbach model based on solution diffusion theory is used. The Rautenbach

solution–diffusion model used in this study, works with transport coefficient instead of diffusion coefficient because its concentration dependence is considered negligible<sup>10</sup>.

The molar flux of component k through the composite membrane can be calculated using Eq.(1)

$$J_K = \frac{1}{1 + \frac{\bar{D}_K}{Q_0 P_{K0} \bar{\gamma}_K}} \cdot \frac{\bar{D}_K}{\bar{\gamma}_K} \cdot \frac{(P_{K1} - P_{K3})}{P_{K0}} \quad (1)$$

Where  $\bar{D}_K$  is the concentration independent transport coefficient of component k,  $Q_0$  is permeability of non supportive porous layer,  $P_{K0}$  is vapor pressure of component at feed temperature,  $P_{K1}$  and  $P_{K3}$  are the partial pressure of component k in the feed and permeate respectively  $\bar{\gamma}_K$  is the average activity coefficient of component k. For high water concentration azeotropes like isobutanol–water separation, this equation needs modification<sup>13</sup>.

Pervaporation is strongly temperature dependent as can be seen in Eq. (2). Transport coefficient depends on the temperature in an Arrhenius type exponential way.

$$\bar{D}_K = \bar{D}_K^* \exp \frac{E_K}{R} \left( \frac{1}{T^*} - \frac{1}{T} \right) \quad (2)$$

$E_K$  represents the activation energy for component k and is associated with the transport coefficient,  $T^*$  is the reference temperature, equal to 293 K. The activity coefficients are calculated with the Wilson equation<sup>13</sup> in this work, but can be calculated with other equation of state models as well. The Wilson parameters were derived from the database of Chemsep software.

A user friendly Visual Basic Simulation program (VBS) was developed, for PV and D+PV model calculations. The VBS tool developed is capable of calculation of Number of Trays, minimum reflux ratio, energy requirement for distillation column, membrane area, energy requirement for different product specifications etc. PV calculations require pervaporation parameters like component diffusivities, activation energies and permeance.

Experimental data reported by Lovasz and coworkers<sup>11</sup> has been used in this study for calculating the component flux through the membrane. Lovasz used commercial membrane PERVAP 2210 (by SULZER Chemtech GmbH) for pervaporation. Data reported for this membrane at 80 °C and 2.7 mbar permeate vacuum has been used in our work. PERVAP 2210 is hydrophilic PVA/PAN (0.5-2 micro meter thick PVA as perm selective and polyacrylonitrile as micro-porous support layer) membrane. The calculation flux was found to be in good agreement for higher ethanol concentration mixture with the reported experimental data (Table I)<sup>11</sup>.

### ***Hybrid Separation Processes for Ethanol-water separation***

Hybrid process configuration coupling membrane separation and distillation studied in current work is presented in Fig. I. Ethanol rich distillate is condensed partly refluxed and the remaining passed

through a pervaporation unit. As the membrane is hydrophilic, water permeates through whereas ethanol remains as the retentate. The bottom product of the distillation unit is predominantly water. Ethanol-water is conventionally separated by heterogeneous azeotropic distillation using n-pentane as entrainer. Separation using Chemcad simulation tool is shown in Fig. The operating cost due to the introduction of the entrainer *N*-pentane and its subsequent separation and recycle in azeotropic separation process are eliminated in the hybrid process.

## **RESULTS AND DISCUSSION**

A comparison of azeotropic distillation and pervaporation for similar feed mixture (128.19 kmol.h<sup>-1</sup>, 85.6% (mol) ethanol) and product purity (103.48 kmol.h<sup>-1</sup>, 99.99% (mol) ethanol) has been carried out initially. The azeotropic distillation, simulated using Chemcad simulator. The reboiler energy input required is 12949 MJ.h<sup>-1</sup>.

Pervaporation (PV) simulated with the VBS program, using PERVAP 22108 membrane is compared with azeotropic distillation in Table II. For achieving similar product purity and output as that of azeotropic distillation, PV requires only 1558 MJ.h<sup>-1</sup> of energy (latent heat and energy for vacuum generation). As no entrainer is used, there is no the requirement of its separation and recycle. However, the process requires a PV unit with membrane area 867 m<sup>2</sup>.

Separation of dilute solutions by pervaporation is not economic due to large membrane surface requirement. The calculations using VBS reveal that a single pervaporation unit of membrane area 3221 m<sup>2</sup> is required to produce 109.44 kmol.h<sup>-1</sup> (99.99 % (mol) ethanol) from 548.89 kmol.h<sup>-1</sup> (20 % (mol) ethanol) and the energy requirement is 37389 MJ.h<sup>-1</sup>. If hybrid separation (D + PV) is used for same, energy requirement reduces to 22100 MJ.h<sup>-1</sup>. Distillation tower with 22 trays and pervaporation unit with membrane area 841 m<sup>2</sup> is sufficient to meet the requirement. Membrane area is reduced by 74 % when hybrid separation (D + PV) is used for separation instead of just pervaporation.

A comparison of the performance of a conventional distillation column and a D+PV hybrid unit for the same feed ethanol concentration (20 % (mol)) is presented in Fig. II. For same number of distillation column trays, product (ethanol mol %) in distillation process and hybrid process is compared and The figure clearly illustrates the advantage of having a hybrid unit for the separation. While the distillation tower composition cannot cross the azeotrope point due to thermodynamic barrier, high purity ethanol can be obtained with a D+PV hybrid unit using a small distillation unit containing lesser number of trays.

### ***Optimum number of trays for Distillation column in hybrid unit***

For the distillation of azeotropes in a conventional distillation unit without entrainer, the number of trays required for distillation increases rapidly as the concentration approaches azeotrope composition. This is depicted in Fig. III, where  $dt/dm$  is the incremental increase in the number of distillation trays with incremental increase in the ethanol concentration at the distillation column outlet and  $m$  the mole fraction of ethanol in the product. The figure shows that there is rapid increase in the number of trays beyond an outlet ethanol concentration of 86.5 % (mol). So it becomes important to judiciously choose the number of trays in the distillation column of the D+PV hybrid unit. The figure indicates that in D + PV hybrid separation unit, it is advantageous to introduce PV unit at a tray composition of about 86 % (mol) instead of the azeotrope point (89.2 % (mol) ethanol).

Once the PV unit location is obtained from the  $dm/dt$  plot, it can be further refined by a combination of the total energy requirement and the number of distillation trays. This is demonstrated in Table III. As ethanol in the distillate increases from 84% to 89%, the number of trays increases and the product composition from PV unit also increases. While the increase in permeate composition is marginal, the increase in the number of trays is significant. There is a 3-fold increase in the number of trays when the distillate composition is increased from 86 to 88 %. The total energy requirement for the hybrid system decreases and passes through a minimum for the distillate composition of 88%. However there is an inordinate increase in the number of trays when the distillate composition is increased from 86 to 88 %. Hence the number optimum number of trays of the Distillation unit is 21 and location of the PV unit is above tray no. 21

### **CONCLUSION**

A comparison of conventional distillation unit, azeotropic distillation unit, pervaporation unit and a hybrid separation unit comprising of distillation and pervaporation has been presented in this paper. Ethanol-water binary separation has been chosen as the model system for the study. A Visual Basic Simulation tool based on material and energy balance calculations and vapour-liquid equilibrium data was used for distillation simulation while Rautenbach model based on solution-diffusion theory has been used for pervaporation calculations. Chemcad software was used for simulation of azeotropic distillation. For calculation of energy requirements, only the reboiler and vacuum pump were considered. The material balance of ethanol for azeotropic distillation shows that there is an overall loss of 5.74% ethanol per hour, whereas the corresponding loss in a pervaporation unit with 867 m<sup>2</sup> membrane area is less than 0.1%. The energy requirement for pervaporation is also considerably less. 80 % energy saving is possible in this case. While it is not possible to obtain ethanol purity above the azeotrope composition in a conventional distillation

tower, by attaching a PV unit after the condenser in conventional distillation, it is possible to obtain very high purity ethanol as product. 40% energy can be saved using hybrid distillation/pervaporation process.

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**Table No. I : Comparison of flux calculated using the VBS and Lovasz's data<sup>8</sup> for ethanol dehydration using PERVAP2210 at different feed ethanol concentrations: Water –  $Q_0$ : 3.0 kmol. m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>,  $D_K^*$ : 4.49\*10<sup>-3</sup> kmol. m<sup>-2</sup> h<sup>-1</sup>,  $E_K$ : 46165 kJ.kmol<sup>-1</sup>. Ethanol –  $Q_0$ : 3.0 kmol. m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>,  $D_K^*$ : 4.63\*10<sup>-6</sup> kmol. m<sup>-2</sup> h<sup>-1</sup>,  $E_K$ : 22614 kJ.kmol<sup>-1</sup>**

Ethanol in Feed (mol %)	Permeate Flux (kmol.m <sup>-2</sup> h <sup>-1</sup> )	Permeate Flux <sup>8</sup> (kmol.m <sup>-2</sup> h <sup>-1</sup> )
82	0.0272	0.03
75	0.04	0.042
70	0.0489	0.0475

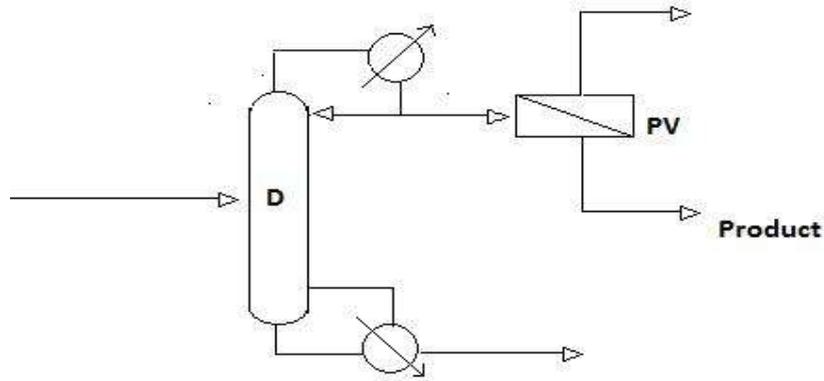
**Table No II :Comparison of azeotropic distillation and pervaporation for ethanol-water system: Feed 128.19 kmol.h<sup>-1</sup>, 85.64 % (mol) ethanol; Product: 103.48 kmol.h<sup>-1</sup>, 99.99 % (mol) ethanol**

Features	Azeotropic distillation	Pervaporation
No. of trays	19	-0-
Entrainer	N-Pentane	Nil
Membrane area (m <sup>2</sup> )	No membrane	867
Energy required (MJ.h <sup>-1</sup> )	12949.00	1558.24

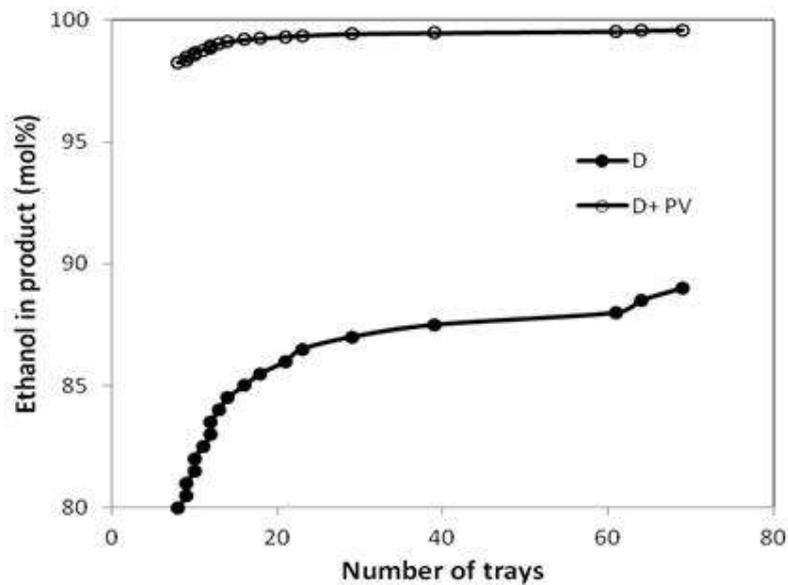
**Table III The effect of PV location on the energy requirement of the (D + PV) hybrid unit. Membrane area used = 1400 m<sup>2</sup>**

Distillate composition (mol % ) at pervaporation feed point	Reflux ratio	Number of trays in distillation tower	Ethanol concentration in retentate (mol %)	Total energy required (D+PV) (kW)
82	4	10	98.67	13292.2
84	4	13	99.02	12866.17
86	4	21	99.33	12461.2
88	4	61	99.54	12068.57
89	6.5	69	99.6	17473.56

**Figure I: Configuration of a hybrid process coupling distillation and pervaporation (D+PV)**



**Figure II Comparison of the performance of a distillation unit and a D+PV hybrid unit for ethanol-water separation for a feed ethanol concentration of 20 % (mol)**



**Figure III: Incremental variations in the number of trays with incremental increase in outlet ethanol concentration (dt/dm) as a function of mole fraction ethanol (m) at the outlet in a distillation tower for the distillation of ethanol-water system without any entrainer**

