Modeling and Simulation of Distillation + Pervaporation Hybrid Unit: Study of IPA - Water Separation

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Abstract : The chemical industry consumes large amount of energy sources to process raw materials. With rising energy prices and increased focus on efficiency, the development of alternative separation processes to conventional separation processes is essential. Although distillation has widespread use in the chemical industry, separations involving close boiling or azeotropic compositions are not feasible in conventional units. Azeotropic distillation with entrainer is a commonly used technique for separation of the mixture iospropanol/water. The separation is not feasible with conventional distillation due to presence of an azeotrope. In this paper, the design of hybrid process consisting of distillation and pervaporation is elaborated as an alternative for the separation and evaluated from energy point of view. Separation of isopropanol/water mixture is carried out by Distillation-Pervaporation (D + PV) hybrid unit. The results clearly reveal the advantage of using a hybrid unit in place of conventional distillation unit. Separation of dilute solutions by pervaporation is not economic due to large membrane surface requirement. At low feed isopropanol concentrations, hybrid separation is more attractive compared to only pervaporation.
Key Words : Hybrid Separation, Distillation, Pervaporation.

Introduction:

Distillation is a widely used method for separating mixtures and is based on differences in the boiling points of the components of the mixture. The separation of liquid mixture in a distillation column is carried out based on the differences in volatility. Today it is recognized as the heart of many process industries. However, azeotropic or constant boiling mixtures separation is difficult by conventional distillation.

Distillation is an energy intensive method for separation. With rising energy prices and increased focus on efficiency, the development of alternative separation processes to conventional separation processes is essential. Membrane technologies have seen a significant growth and increase in application in the last two decades. Pervaporation is the separation method based on selective evaporation and is used to separate one of the components of a liquid mixture using a membrane. This phase change is usually obtained by lowering the partial pressure of permeates at the down-stream side of the membrane by vacuum[1]. Moreover pervaporation generally requires less energy as compared with other competitive processes including distillation. By replacing distillation by the pervaporation membranes or combining the two processes large energy savings are possible. However, to completely replace distillation with pervaporation may not be economically viable for most large scale operations because of huge membrane areas required. The major factor affecting the cost of pervaporation is the membrane area due to which it is uneconomical to use pervaporation alone for high product purity[2].

Hybrid processes are very promising especially in cases where high product purities are required. These hybrid processes can be applied for the separation of azeotropic mixtures without use of any entrainer. The combination of pervaporation and distillation in hybrid processes has shown attractive energy-saving possibilities in many cases[3]. In case of Acetic acid water separation using distillation/pervaporation hybrid process energy gain upto 20 % is achievable[4]. Savings in total annual cost upto 12% can be achieved using hybrid separation process[5]. Hybrid systems of different types reduce energy expenditures, make liquid mixture separations that are otherwise difficult, and/or improve the degree of separation[6,7]. Combined processes consisting of distillation and pervaporation/ vapour permeation offers economically attractive alternatives as they can simplify the process structure, reduce the energy consumption and avoid entrainers[7].High purity ethanol cannot be obtained through simple distillation because of azeotrope formation. In this paper we explore this idea using ethanol-water as the model system and separation using a combination of distillation (D) and pervaporation (PV).

Theory:

A mathematical model of the distillation column with a total condenser and a partial reboiler was developed. The model includes mass and energy balances at each tray, coupled with vapor-liquid equilibrium relationship. It uses UNIQUAC and Virial equations of state [8] to represent the vapor liquid equilibrium (VLE) of the mixture. Mccabe-Thiele[9] method is used for calculation of number of trays required for distillation tower.

Pervaporation:

Among the diverse pervaporation models described in literature, the most widely used is the solution diffusion model[10]. The solution-diffusion model provide an accurate description of the behavior of membranes and the dependence of membrane transport on pressure, concentration and the like[10,11]. According to this model, the transport occurs in three steps. First step is selective sorption of the components on the membrane surface. Second step is diffusion of the components through the membrane and third step is desorption to the permeate side.

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 permeate of the component through porous layer flows by diffusive or pore flow. Chemical potential difference between the feed and the permeate sides is the driving force for the transport through the membrane. The pressure through the membrane material is assumed to be constant so that the chemical potential gradient gets simplified to concentration gradient.

The process of separation by pervaporation originates in the solution–diffusion principle[10]. Luyben [5] developed a simple pervaporation model based on diffusivities for study of a column/pervaporation process control. For our study, Rautenbach model based on solution-diffusion theory is chosen. The Rautenbach solution–diffusion model uses the fugacity gradient instead of the chemical potential gradient between the two sides of the membrane. The Rautenbach model works with transport coefficient instead of diffusion coefficient because its concentration dependence is considered negligible[12]. Other developed models were focused on different membrane modules as compared to earlier models which are based on membrane properties[13,14].

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

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

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.

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

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

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. In generally, it can be seen the lower is the composition of feed mixture and the higher the operating temperature, the better is the separation capability of the membrane[6].The activity coefficients are calculated with the Wilson equation 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.

Process simulation software:

In this study 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 Csefalvay and coworkers[15] has been used in this study for calculating the component flux through the membrane. Csefalvay used commercial hydrophilic flat sheet membrane PERVAP 2210 (by SULZER Chemtech GmBh) for pervaporation. Data reported for this membrane at 80 ^{0}C and 2.64 mbar permeate vacuum has been used in our work. PERVAP 2210 is hydrophilic PVA/PAN (0.5-2 micro meter thick PVA as permselective and polyacrylonitrile as micro-porous support layer) membrane.

Azeotropic and Hybrid Separation Processes for Isopropyl alcohol-water separation:

Isopropyl alcohol-water is conventionally separated by azeotropic distillation using cyclohexane as entrainer. A schematic diagram of azeotropic distillation process is presented in Fig. 1. In this isopropyl alcohol-water mixture and make up cyclohexane enters the distillation column. The distillate is rich in cyclohexane and the bottom product is 85 mol % isopropyl alcohol. The distillate enters a flash drum where it separates into two layers. Most of the water in the distillate along with some isopropyl alcohol gets separated at the bottom and is purged out. The side product from the flash drum is high on cyclohexane, contains some isopropyl alcohol and is recycled to the distillation column.
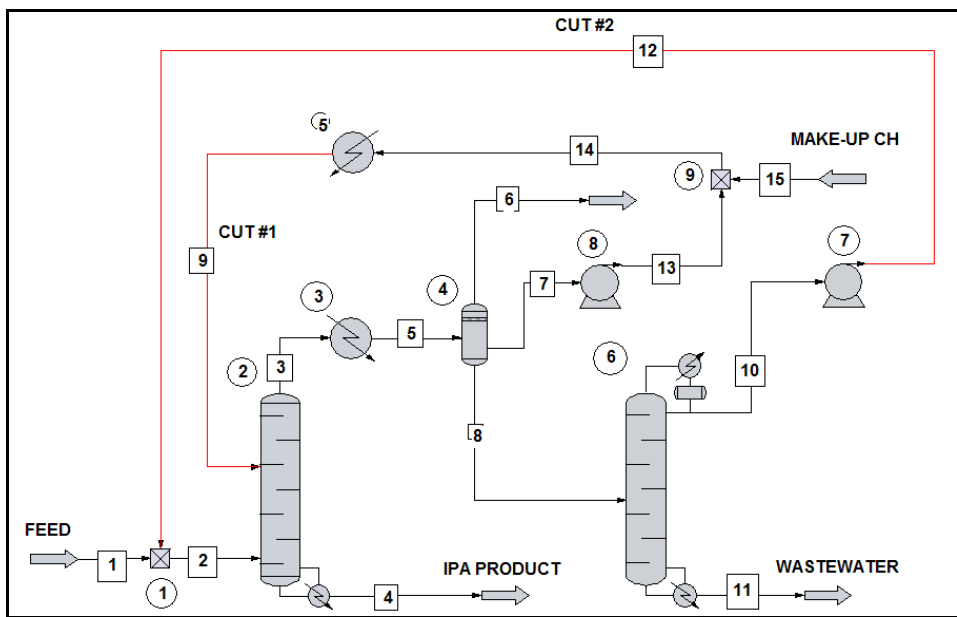
Stream/Flows	Unit Operations/Others
1 : Feed mixture	**1** : Mixer
2 : IPA-water mixture	**2** :Distillation column 1
3 : Top distillate product	**3** :Heat Exchanger
4 : Bottom product (IPA)	**4** :Flash drum
5 : Inlet stream to flash drum	**5** :Heat Exchanger
6 : Vent	**6** : Distillation column 2
7 : Purge (most of the water gets separated)	**7** : Centrifugal Pump
8 : Side stream from flash drum (major composition n-pentane)	**8** : Centrifugal Pump
9 : Recycled stream to distillation column	**9** : Mixer
10 : Distillate from column 2 to be recycled to column 1	
11 : wastewater from column 2	
12 : Distillate from column 2 to be recycled to column 1 (with high pressure)	
13 : Side stream from flash drum (high pressure)	
14 : Stream No. 13 added with makeup cyclohexane	
15 : makeup cyclohexane	

Figure 1: Schematic of Azeotropic distillation (using Chemcad)

Hybrid process configuration coupling membrane separation and distillation studied in current work is presented in Fig. 2. IPA rich distillate is condensed, partly refluxed and the remaining passed through a pervaporation unit. As the membrane is hydrophilic, water permeates through whereas IPA remains as the retentate. The bottom product of the distillation unit is predominantly water. The operating cost due to the introduction of the entrainer *n*-pentane and its subsequent separation and recycle are eliminated in the hybrid process.
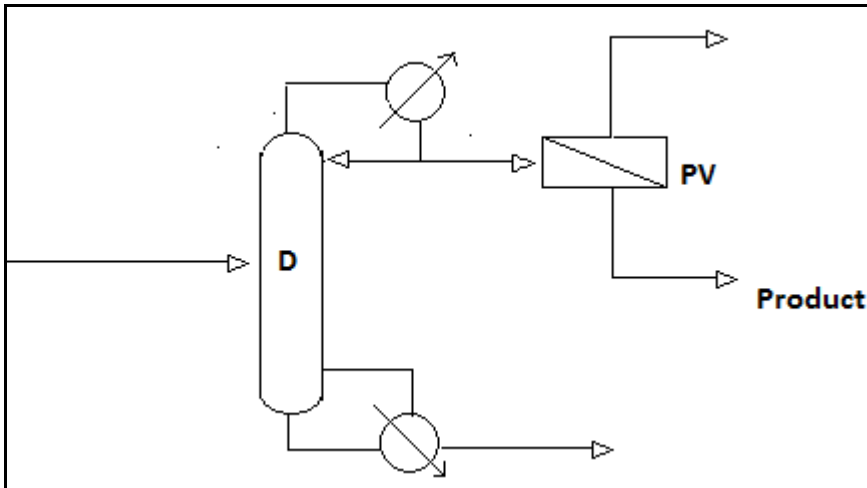
Figure 2: Configuration of a hybrid process coupling distillation and pervaporation (D+PV)
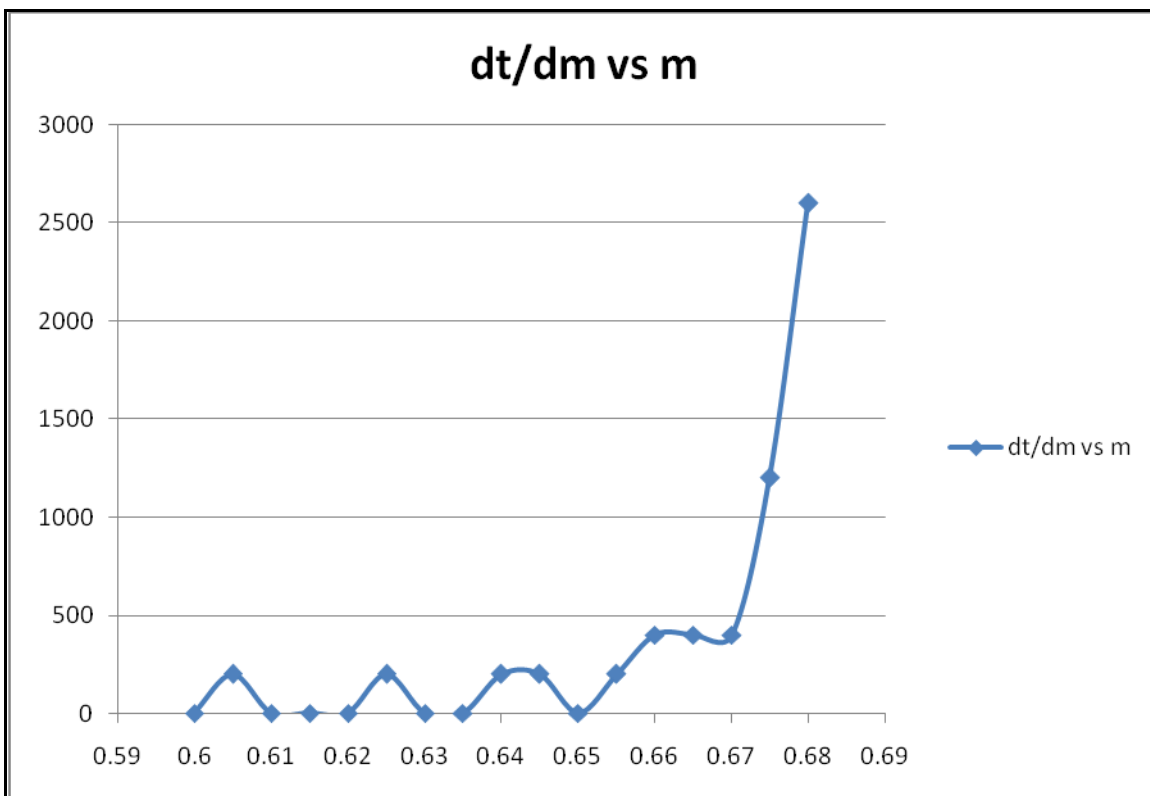

Figure 3: Incremental variations in the number of trays with incremental increase in outlet IPA concentration (dt/dm) as a function of mole fraction IPA (m) at the outlet in a distillation tower for the distillation of IPA-water system without any entrainer.

Results and Discussion

A comparison of azeotropic distillation and pervaporation for similar feed mixture (831.406 kmol.h^{-1}, 62.95% (mol) isopropyl alcohol) and product purity (615.05 kmol.h^{-1}, 85.06% (mol) isopropyl alcohol) has been carried out initially. The azeotropic distillation, simulated using Chemcad simulator uses cyclohexane as entrainer, has two distillation columns and has no PV unit. The distillate composition is IPA: 34.7%, cyclohexane: 46.8% and water: 18.6%. The bottom product is 85 % IPA. The distillate is passed into a flash drum where it separates into two layers. The water rich bottom product contains water: 89.82%, IPA: 10% and cyclohexane: 0.1%. Side product from flash drum having composition (cyclohexane: 53.7%, water: 7.9 % and IPA: 38.3 %) is recycled to distillation column. The reboiler energy input required for this operation is 65726.04 MJ.h^{-1}. The water rich bottom product from flash drum enters in second distillation column. Distillate

composition from 2'nd column is IPA: 65.71%, cyclohexane: 1% and water: 33.27%. The bottom product is 99.9 % water. The reboiler energy input required for this separation is 9567.55 MJ.h-1. Total energy input for azeotropic distillation process is 75293 MJ.h-1. Pervaporation (PV) simulated with the VBS program, using PERVAP 2210[12] membrane is compared with azeotropic distillation in Table 2. For achieving similar product purity and output as that of azeotropic distillation, PV requires only 17736 MJ.h^{-1} of energy (latent heat and energy for vacuum generation). As no entrainer is used, there is no requirement of its separation and recycle. However, the process requires a PV unit with membrane area 4400 m^2.

Table 1 The effect of PV location on the energy requirement of the (D + PV) hybrid unit. Membrane area used = 1400 m^2

Distillate composition (mol %) at pervaporation feed point	Reflux ratio	Number of trays in distillation tower	IPA concentration in retentate (mol %)	Total energy required (D+PV) (MJ)
63	1.5	6	81.35	37193.01
64	1.5	7	82.24	36515.23
65	1.5	8	83.12	35854.66
66	1.5	11	83.96	35211.04
67	1.5	15	84.78	34583.51
68	1.5	34	85.52	33959.58

Table 2 Comparison of azeotropic distillation and pervaporation for IPA-water system: Feed 831.406 kmol.h^{-1}, 62.95 % (mol) IPA; Product: 615.05 kmol.h^{-1}, 85.06% (mol) IPA.

Features	Azeotropic distillation	Pervaporation
No. of trays	19	-0-
Entrainer	cyclohexane	Nil
Membrane area (m^2)	No membrane	4400
Energy required (MJ.h^{-1})	75293.00	17736

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 5534 m^2 is required to produce 684.52 kmol.h^{-1} (85% (mol) IPA) from 1000 kmol.h^{-1} (58.5 % (mol) IPA) and the energy requirement is 25696.8 MJ.h^{-1}.

For achieving 615.22 kmol (85 mol % IPA) solution from 1308 kmol (20 mol% IPA) dilute solution, azeotropic distillation requires 158720 MJ.h^{-1} energy. Whereas for same, Distillation+ pervaporation requires 101163 MJ.h^{-1} energy.

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. IPA-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.

While it is not possible to obtain IPA 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 IPA as product. Calculations reveal that 36% energy can be saved using D+PV process configuration over the azeotropic distillation process.

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