

Modeling and Simulation of a Hybrid Process (Pervaporation+Distillation) using MATLAB

Sohail Rasool Lone^{*1}, Syed Akhlaq Ahmad² and Vimal Kumar¹

¹Chemical Engineering Department, IIT Roorkee, Roorkee-Uttarakhand, India

²Chemical Engineering Department, Aligarh Muslim University Aligarh, U.P, India

Abstract

This paper reports the modeling and simulation of a hybrid process, based on the combination of distillation and pervaporation, for the separation of azeotropic mixture of alcohol and ether. Pervaporation has emerged as one of the most active areas in the membrane research, and the pervaporation process has been shown to be an indispensable component for chemical separations. Pervaporation is more suitable for the separation of azeotropic or constant boiling mixtures which otherwise are difficult to separate by ordinary distillation. Although distillation is the most widely used technique for the separation of liquid mixtures, however the distillation separation of the mixtures with an azeotropic composition or close boiling mixtures is energetically expensive. A hybrid process exploits the advantages of pervaporation and distillation, while the negative aspects are minimized. Simulation tasks were carried out with MATLAB and the results of alternative process configurations that result from the relative location of separation technologies have been compared on the basis of the required membrane area.

Keywords: Modeling; Simulation; Distillation; Pervaporation; Hybrid process

Nomenclature

F: Molar flow rate of the feed (kmol/hr);
 $f_{i,j}$: Feed flow rate of component 'i' (kmol/h);
 D: Total molar flow rate of distillate [kmol/hr];
 B: Total molar flow rate of bottom [kmol/hr];
 Rr: Reflux ratio;
 N: Number of stages in the column;
 Nf: Stage at which feed enters the column;
 Lj: Total molar flow rate at which liquid phase leaves jth stage (kmol/h);
 Vj: Total molar flow rate at which vapour phase leaves jth stage (kmol/h);
 Wj: Molar flow rate of the vapour side stream leaving jth stage (kmol/h);
 Uj: Molar flow rate of the liquid side stream leaving jth stage (kmol/h);
 $l_{i,j}$: Molar flow rate of component 'i' in the liquid phase leaving jth stage (kmol/h);
 $v_{i,j}$: Molar flow rate of component 'i' in the vapour phase leaving jth stage (kmol/h);
 $z_{i,j}$: Mole fraction of component 'i' in the feed stream entering jth stage;
 $x_{i,j}$: Mole fraction of component 'i' in the liquid phase leaving jth stage;
 $y_{i,j}$: Mole fraction of component 'i' in the vapour phase leaving jth stage;
 Ji: Flux of component 'i' through the membrane (kmol/(m².s));
 $x_{i,j}$: Molar composition of component 'i' in retentate(j=1) and

permeate(j=2);
 DMTBE: Diffusivity of the MTBE (m²/s);
 DMeOH: Diffusivity of the methanol (m²/s);
 D0: Intrinsic diffusivity of the methanol (m²/s);
 $k_{i,j}$: Parameters used in the adsorption model;
 P2: Pressure of the permeate side (Pa);
 $P_i V$: Vapour pressure of the component 'i', (Pa);
 zp: Membrane thickness coordinate (m);
 m: Mass flow rate i.e mass per unit time (Kg/s);
 W: Characteristic membrane width (m);
 L: Characteristic membrane length (m);
 Tj: Temperature at the jth stage (K);
 zA: Membrane length coordinate (m);
 hF: Enthalpy of the feed [J/(kmol.K)];
 hL: Enthalpy of the liquid [J/(kmol.K)];
 hV: Enthalpy of the vapour [J/(kmol.K)];
 sw: Fraction of the liquid withdrawn from the column;
 Yi: Activity coefficient for component 'i' obtained with a gE model;
 ϕ_i : Volumetric composition of component 'i' within the membrane;

***Corresponding author:** Sohail Rasool Lone Chemical Engineering Department, IIT Roorkee, Roorkee-Uttarakhand, India, Tel:911332285 311; E-mail: lonesohail92@gmail.com

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τ : Plasticizing coefficient;
 ρ_i : Liquid density of component 'i'(kmol/m³);
 ζ : Membrane thickness(m);
 λV : Heat of vaporization (J/kmol);
 ψ : Vapor Fraction of the feed ($\psi=V/F$);
i: Component;
j: Stage;
k: Counting number;
L: Liquid phase;
V: Vapor phase;
MeOH: Methanol;
MTBE: Methyl-tertiary butyl ether

Introduction

The phase-out of lead antiknock compounds in gasoline has fostered a great interest to the use of ethers as an alternative to octane enhancers. Among them, methyl tertbutyl ether (MTBE) appears to be both a good octane enhancer and an excellent oxygenated fuel additive needed for the reformulation of gasoline. For these reasons, demand for MTBE is increasing. The increasing frequency of detection of MTBE in both ground and surface waters is receiving much attention in the U.S. (especially in California), and some environmental and political groups are calling for an immediate ban. However, the other groups feel that eliminating MTBE would be like treating a symptom and not the disease that the MTBE in the drinking water is an indicator of a bigger problem; leaking storage tanks. Thus, the best and the most effective solution would be simply fixing the tanks. On the other hand, in Europe, MTBE consumption is expected to increase. Limiting aromatics will drastically affect the refining blending pool. Thus, European refiners will have to use MTBE to produce octane-graded gasoline. The production process of MTBE involves the separation of MTBE, mixed C₄'s and un-reacted methanol from the reactor effluent to achieve a high purity MTBE, but unfortunately the un-reacted methanol (MeOH) forms azeotropic mixtures with both MTBE at 14.3 wt% MeOH and 760 mmHg and with butenes that are difficult to separate by distillation. This fact makes the conventional method both expensive and energy intensive. Pervaporation has proven to present a high potential separation alternative, because it is less energy consuming than distillation. The pervaporation operation is a separation technique based on the selective transport through a dense layer associated with evaporation of permeates. This phase change is usually obtained by lowering the partial pressure of the permeates at the down-stream side of the membrane by vacuum [1].

Hybrid Process (Pervaporation+Distillation)

It has been widely recognized that membrane separation processes can offer many advantages as compared to conventional mass transfer processes. A large number of membrane separation processes are currently being practiced in various sectors of industries. Despite the advantages, membrane processes often suffer from shortcomings when used individually. To overcome such limitations, membrane based hybrid processes have been developed to maximize the productivity of the target separation processes.

Membrane technologies have recently emerged as an additional

category of separation processes to the well-established mass transport processes. Membrane separation technologies offer various advantages over existing mass transfer processes like high selectivity, low energy consumption, moderate cost to performance ratio and compact and modular design.

However, membrane processes have several inherent limitations. For example, a membrane system designed to treat waste water may be limited by the water's osmotic pressure, viscosity, temperature and high concentration of suspended solids. Therefore, the optimal separation process in many cases may be a 'Membrane-based hybrid process' that combines either a membrane process with a conventional process or a membrane process with the other membrane process. A hybrid process is appropriate when it offers significant advantages such as lower capital and production costs or reduced energy requirements over the exclusive use of conventional processes. Hybrid processes like combination of distillation and pervaporation are very promising especially in cases when high product purities are needed. Pervaporation seems to be especially suited for the separation of azeotropic or similarly boiling organic or aqueous-organic mixtures [2].

In most of the hybrid configurations, distillation is more economical for the bulk of the separation, while the membrane is used to perform the part of separation, where distillation is difficult or impossible. Several kinds of hybrid configurations have been studied. In general, the pervaporation module can be used in a hybrid distillation system to remove specific component from a lateral stream of the distillation column, e.g. to overcome the azeotropic composition or as a final treatment stage. More recently, the hybrid processes integrating pervaporation with other variable liquid separating technologies are gaining momentum. With these developments, we have more reasons to believe that hybrid processes will play even more important roles in future.

Advantages of Hybrid Processes

- Hybrid processes like combination of distillation and pervaporation are very promising especially in cases where high product purities are required.
- To reduce costs, particularly energy costs, make possible a difficult separation, and/or improve the degree of separation, hybrid systems, consisting of two or more separation operations of different types in series are used.
- Hybrid systems of different types reduce energy expenditures, make separations that are otherwise difficult, and/or improve the degree of separation [3].

Pervaporation Model

There is no universal model capable of predicting the behavior of pervaporation process for any component; thus particular considerations have to be made to adequately represent the process for each different mixture, yielding as many models as mixtures to separate. The equations for modeling such a system are highly dependent on the components to be processed in the pervaporation membrane, hence the importance of comparing the experimental results with those given by the model used to predict the fluxes and compositions [4].

Generally, the model used for pervaporation membrane module assumes that the mechanism of pervaporation through dense polymer membranes can be divided into three stages; the components are first adsorbed over the membrane layer, then they diffuse through the membrane and finally they desorb at the other side of the membrane.

The process of transport is very complex, because of the interactions between the components and the membrane itself; however the proposed mechanisms of transport can be roughly divided into two types; sorption-diffusion models and models of flux into pores. In our case, the pervaporation is essentially described using a complex sorption-diffusion model to represent the behavior of the components as they pass through the membrane (Figure 1).

If the rate limiting step is transport through the membrane, the approach of using the generalized Fick's law, a mathematical model for describing the pervaporation fluxes in the membrane, developed by [5] and further improved by [6,7] can be used. The model can be extended to multi-component mixtures if the experimental data are available to determine the required parameters. The key is to find the governing mechanism for the mass transport through the membrane and a model that can adequately represent the behavior of each component in the pervaporation process.

The modeling for the pervaporation process for a mixture of methanol and MTBE (methyl tert-butyl ether) has been discussed here. This however does not limit the scope of this study; in fact, if the experimental data are available, equations for other systems following a sorption-diffusion model can be posed similarly just by finding the best way of predicting the diffusion coefficient. This is a semi-empirical model, because the parameters must be found experimentally. The geometry used for the pervaporation membrane module is plate and frame, thus having a characteristic membrane width 'W' and a membrane length 'L' for commercial membranes of known area 'A'. The membrane has a known thickness, zeta 'ξ'. A simplified schematic of the pervaporation module has been shown in Figure 1.

The flux 'J' through the membrane is given by (Equation 1):

$$J(c, T) = J_{\text{total}}(c, T) = \sum_i J_i(c, T) \quad (1)$$

Where 'c' is the vector of mass compositions (i=1 for methanol and i=2 for MTBE); J_i is the flux of component 'i', and T is the absolute temperature (K). Experimental data have been obtained for the fluxes of both the components and it has been determined that the prediction of the flux of methanol requires a concentration-dependent diffusion-coefficient, whereas a simple model with concentration independent diffusivity is sufficient for defining the MTBE flux. Taking into account these considerations, the resulting equations for the prediction of pervaporation fluxes for one membrane module are (Equation 2 and 3,4):

$$J_1(c, T) = -D_{\text{MeOH}} \rho_1 \frac{d\phi_1}{dz_p} \quad (2)$$

With

$$D_{\text{MeOH}} = \frac{D_0 \phi_1 \exp(\tau \phi_1) k_{2,1}}{[(k_{2,1} \phi_1 + 1) \ln(k_{2,1} \phi_1 + 1)]} \quad (3)$$

$$J_2(c, T) = -D_{\text{MTBE}} \rho_2 \frac{d\phi_2}{dz_p} \quad (4)$$

The boundary conditions are as follows (Equation 5-9):

At $z_p=0$,

$$\phi_1 = \frac{[\exp(\gamma_1 x_{1,1} / k_{1,1}) - 1]}{k_{2,1}} \quad (5)$$

$$\phi_2 = \frac{\gamma_2 x_{2,1}}{k_{1,2}} \quad (6)$$

At $z_p=\xi$

$$\phi_1 = \frac{\{\exp[P_2 x_{1,2} / P_1^v(T) k_{1,1}] - 1\}}{k_{2,1}} \quad (7)$$

$$\phi_2 = \frac{P_2 x_{2,2}}{P_2(T) k_{1,2}} \quad (8)$$

Global mass balance:

$$\frac{-d_m}{dz_A} = AJ(c, T) \quad (9)$$

Where $z_A = \frac{z}{L}$ is the dimensionless length of the membrane and 'A' is the area of the membrane.

Component mass balance (equation 10):

$$\frac{-dc_i}{dz_A} = \frac{[\beta_i(c, T) - 1] c_i J(c, T) A}{m} \quad (10)$$

As the temperature is not constant, the energy balance is also required (equation 11);

$$\frac{-dT}{dz_A} = \frac{[AJ(c, T) \lambda_v(c, T)]}{m C_{pL}(c, T)} \quad (11)$$

Various Assumptions in Pervaporation Model

A mathematical model of a plate and frame module (Figure 1) was developed, where the above membrane performance was incorporated. Steady-state mass and energy balance were developed considering, (i) plug flow for the free liquid stream, (ii) perfect mixing in permeated vapor, (iii) maximum efficiency in the module (100%), (iv) negligible pressure drop within the module, (v) negligible polarization effects and (vi) negligible heat losses.

Various Assumptions in Distillation Model

- No chemical reaction occurs.
- The energy balance is based on the conservation of enthalpy instead of internal energy.
- Perfect mixing in both phases at each stage.
- Thermal and thermodynamic equilibrium between the phases at each stage. Murphree efficiencies may be applied.

Distillation Model

In order to screen combinations of design and operating variables, a mathematical model of the distillation column, including a total

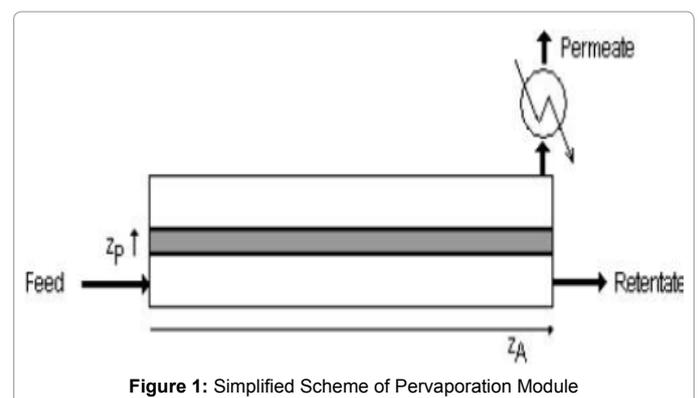


Figure 1: Simplified Scheme of Pervaporation Module

condenser and a partial reboiler, was developed. The model includes mass and energy balances on each stage, coupled with vapor-liquid equilibrium relationships. The distillation column is described by a group of equations that model the equilibrium stages in a column configuration. The equilibrium stage model assumes that vapor and liquid streams leaving a given stage are in thermodynamic equilibrium with each stage. The equations representing the equilibrium stage model are known as MESH equations (Figure 2).

Mass balance

The model equations for a general 'j' stage and component 'i' are represented as (eqn 12):

$$L_{j-1}x_{j-1,i} + V_{j+1}y_{j+1,i} + F_j Z_{j,i} - (V_j + S_j^v)y_{j,i} - (L_j + s_j^l)x_{j,i} = 0 \quad (12)$$

In terms of the flow rate of the components, the above equation can be written as (eqn 13):

$$l_{j-1,i} + v_{j+1,i} + f_{j,i} - v_{j,i} - s_{j,i}^l - l_{j,i} - s_{j,i}^v = 0 \quad (13)$$

Where (eqn 14-19)

$$l_{j,i} = L_j x_{j,i} \quad (14)$$

$$v_{j,i} = V_j y_{j,i} \quad (15)$$

$$V_j = \sum_{i=1}^c v_{j,i} \quad (16)$$

$$L_j = \sum_{i=1}^c l_{j,i} \quad (17)$$

$$s_j = \frac{U_j}{L_j} \quad (18)$$

$$S_j = \frac{W_j}{V_j} \quad (19)$$

Substituting the equations (17)-(22) in equation 13, we get (eqn 20-21):

$$l_{j-1,i} + v_{j+1,i} + f_{j,i} - (l_{j,i}/x_{j,i} + s_j l_{j,i}/x_{j,i})x_{j,i} - (v_{j,i}/y_{j,i} + S_j v_{j,i}/y_{j,i})y_{j,i} = 0 \quad (20)$$

$$l_{j-1,i} + v_{j+1,i} + f_{j,i} - (l_{j,i} + s_j l_{j,i}) - (v_{j,i} + S_j v_{j,i}) = 0 \quad (21)$$

Multiplying the above equation throughout by -1, we get (eqn 22):

$$l_{j,i}(1 + s_j) + v_{j,i}(1 + S_j) - l_{j-1,i} - v_{j+1,i} - f_{j,i} = 0 \quad (22)$$

Equilibrium relationship

The compositions of the streams leaving stage are in equilibrium. Therefore, the mole fractions of the component 'i' in the liquid and vapor streams leaving stage 'j' are related by the equilibrium relation as (eqn 23):

$$y_{j,i} = K_{j,i} x_{j,i} \quad (23)$$

Substituting the equations (14),(17) in equations (23), we get (eqn 24,25):

$$y_{j,i} - K_{j,i} x_{j,i} = 0 \quad (24)$$

$$\frac{v_{j,i}}{V_j} - \frac{K_{j,i} l_{j,i}}{L_j} = 0 \quad (25)$$

Multiplying the above equation throughout by -1, we get (eqn 26):

$$\frac{K_{j,i} l_{j,i}}{L_j} - \frac{v_{j,i}}{V_j} = 0 \quad (26)$$

Now multiplying the above equation throughout by V_j , we get (eqn

27,28):

$$\frac{K_{j,i} l_{j,i} V_j}{L_j} - v_{j,i} = 0 \quad (27)$$

$$K_{j,i} l_{j,i} = \left(\frac{\sum_{k=1}^c v_{k,j}}{\sum_{k=1}^c l_{k,j}} \right) - v_{j,i} = 0 \quad (28)$$

Summation equations

Two additional equations arise from the necessity that the mole fractions of all the components in either vapor or liquid phase must sum to unity (eqn 29,30).

$$\sum_{i=1}^c x_{j,i} = 1 \quad (29)$$

$$\sum_{i=1}^c y_{j,i} = 1 \quad (30)$$

In terms of the flow rate of the components, the above equations can be written as (eqns 31,32):

$$\sum_{i=1}^c l_{j,i} = L_j \quad (31)$$

$$\sum_{i=1}^c v_{j,i} = V_j \quad (32)$$

Energy balance

The total energy balance for stage 'j' is given by (eqn 33):

$$L_{j-1}hL_{j-1} + V_{j+1}hV_{j+1} + F_j hF_j - (L_j + U_j)hL_j - (V_j + W_j)hV_j - Q_j = 0 \quad (33)$$

Now using the equations (14)-(19) in equation (33), a new enthalpy equation in terms of j,i l and j,i v will be obtained as under (eqn 34):

$$hL_{j-1} \sum_{i=1}^c l_{j-1,i} + hV_{j+1} \sum_{i=1}^c v_{j+1,i} + hF_j \sum_{i=1}^c f_{j,i} - (l_{j,i}/x_{j,i} + s_j l_{j,i}/x_{j,i})hL_j - (v_{j,i}/y_{j,i} + S_j v_{j,i}/y_{j,i})hV_j - Q_j = 0 \quad (34)$$

Rearranging the above equation we get (eqn 35):

$$hL_j(1 + s_j) \sum_{i=1}^c l_{j,i} + hV_j(1 + S_j) \sum_{i=1}^c v_{j,i} - hL_{j-1} \sum_{i=1}^c l_{j-1,i} + hV_{j+1} \sum_{i=1}^c v_{j+1,i} - hF_j \sum_{i=1}^c f_{j,i} - Q_j = 0 \quad (35)$$

Two additional equations, which are known as the replacement equations have been used for the stage 1 (Condenser) and stage N (Reboiler), respectively, which are given here as under (eqn 36 and 37):

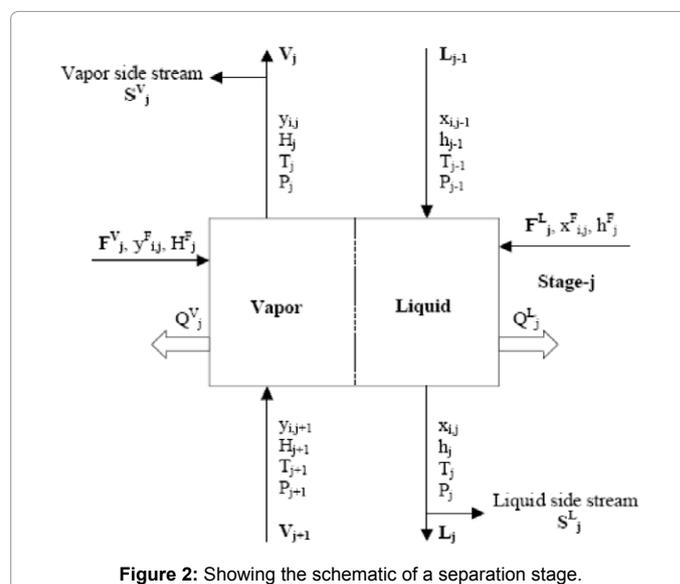


Figure 2: Showing the schematic of a separation stage.

$$\sum_{i=1}^c l_{i,j} - \left(\frac{L}{D}\right) \sum_{i=1}^c v_{i,j} = 0 \quad (36)$$

$$\sum_{i=1}^c l_{N,j} = 0 \quad (37)$$

Hybrid Process (Pervaporation+Distillation) Model

The hybrid model is basically a model which will consist of both these two models i.e. the pervaporation model and the distillation model. There can be actually two different configurations of the hybrid process viz. pervaporation followed by distillation and pervaporation embedded in distillation as shown in Figure 3.

Simulation

Model equations have been developed for the hybrid process (pervaporation+distillation). The model equations for the pervaporation process are simple ordinary differential equations (ode's) of 1st order, whereas the model equations for the distillation are simple algebraic equations, also known as MESH equations. The model equations for the pervaporation process have been solved by making use of ordinary differential equation solver 'ode15s', whereas the model equations for the distillation have been solved by making use of solver 'fsolve' using MATLAB. The two models have been merged together and have been solved under different operating conditions for two different configurations of the hybrid process.

Results and Discussion

Effect of the feed condition

First of all, simulations have been carried out for the distillation column independently without any externally connected pervaporation unit. This has been done in order to study its behaviour, when feed of different types are fed viz. saturated vapor, saturated liquid and 50% vaporized feed, with the design and operation of the column remaining unchanged. By running the simulations for the distillation, it has been actually tried to establish the thermal condition of the feed that leads to a greater methanol concentration in the liquid phase inside the column. The simulation calculations indicate that the latter is obtained by means of feeding a saturated liquid feed, which is beneficial from both the separation and heat economy view point. The results which have been obtained upon the simulation of distillation column are shown here in the form of different plots which are presented here (Figures 4-7).

Figure 4 shows the variation of methanol composition profiles inside the column at different feed conditions. It can be clearly observed from this figure that the maximum methanol concentration in both the rectifying and the stripping section of the column occurs for the saturated liquid feed. This feed condition is therefore considered as an optimum feed condition for the rest of the simulation work. A liquid side draw can be taken from the column at this stage where this peak in methanol concentration occurs inside the column and this side draw can be fed to the pervaporation unit which can be placed parallel to the column so as to remove methanol through the pervaporation membrane which is more selective for methanol as compared to MTBE. In this way, the purity of MTBE can be increased in the bottom of the column.

Figures 5 and 6 shows the effect of feed condition on the composition of the MTBE and Iso-butylene, respectively, inside the column. It can be clearly noticed from these figures that the maximum composition of MTBE in the bottom of the column and that of Iso-butylene in the

top corresponds to the saturated liquid feed. This also confirms that the saturated liquid feed is an optimum feed condition for the present work. Hence, it can be concluded that it is always better to operate the column for saturated liquid for this mixture of methanol/MTBE/Iso-butylene, which is economical from heat economy viewpoint and also from viewpoint of MTBE purity in the bottom of the column. Figure 7 shows the temperature variation along the column. It can be clearly observed that the temperature increases from the top to the bottom of the column. There exists a minimum temperature at the top of the column which is

obvious because of the condenser there at the top through which heat is removed and hence there is minimum temperature and then it increases downwards and shows a sudden increase at the feed stage, because of the feed conditions and the type of the feed and then it increases until it reaches its maximum at the bottom of the column, which is again obvious because of the reboiler there at the bottom of the column. In nutshell, it can be concluded that temperature shows an increasing trend from top to the bottom of the column.

Comparison of the MATLAB

Results with ChemSep simulation

A comparison of the simulation results for the developed model using MATLAB and those obtained by ChemSep Simulation Software have been made. These results are shown in Figures 8-11. These depict a comparison of composition profiles of methanol, MTBE and Iso-butylene and temperature profiles at

different thermal conditions of the feed. It can be clearly observed that there is a close agreement between the two simulation results for the fixed feed composition, but for the different thermal conditions of feed.

Effect of feed composition on MTBE purity

Figure 12 shows the effect of feed composition on the purity of MTBE in the bottom of the column. It can be observed from this figure

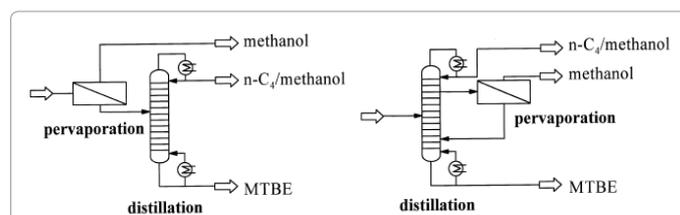


Figure 3: Possible Hybrid Process (Pervaporation+Distillation) Configurations.

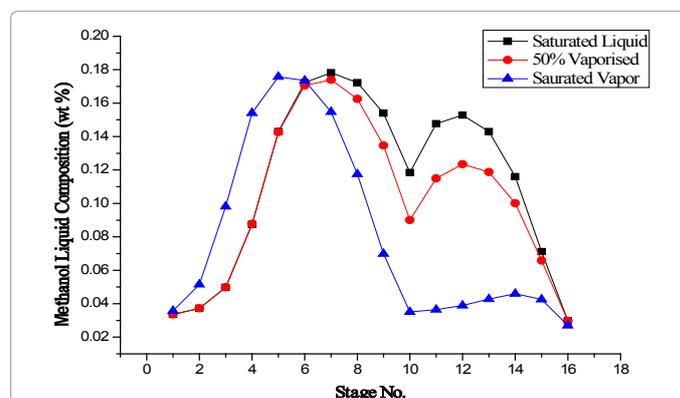


Figure 4: Methanol Liquid Composition Profile in the Column for Varying Feed Conditions.

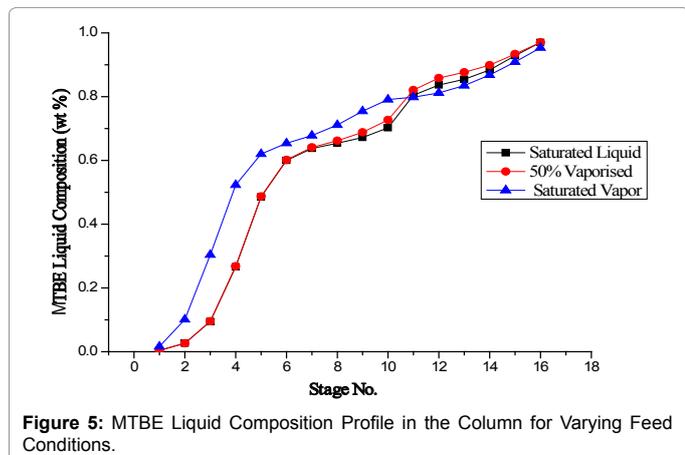


Figure 5: MTBE Liquid Composition Profile in the Column for Varying Feed Conditions.

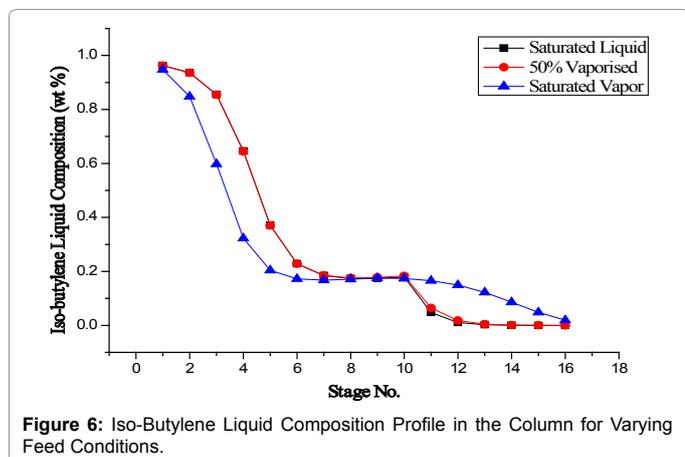


Figure 6: Iso-Butylene Liquid Composition Profile in the Column for Varying Feed Conditions.

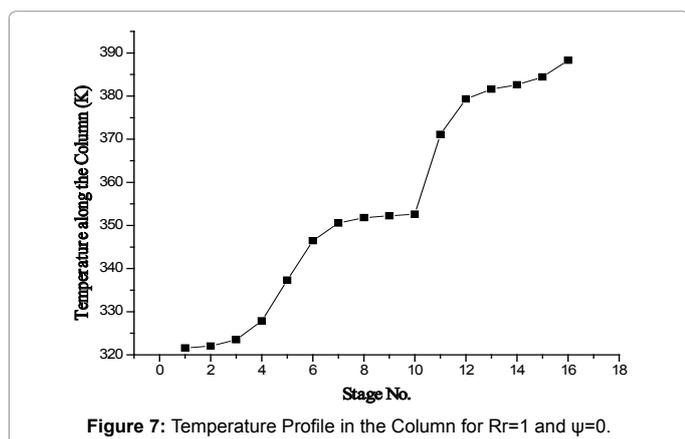


Figure 7: Temperature Profile in the Column for Rr=1 and $\psi=0$.

that the purity of MTBE for feed3 (2.8 wt% MeOH, 25.2 wt% MTBE and 72

wt% i-C4) is maximum among all the three feeds that are fed to the column. It also shows that the purity of MTBE increases in the bottom of the column for the low methanol composition and high i-C4 composition in the feed that is fed to the column, which is clearly evident from the above Figure. It can be concluded that in order to obtain high MTBE purity, methanol concentration must be reduced in the feed or inside the column. The pervaporation provides a better way to accomplish this task. A hybrid process is therefore suggested.

Pervaporation followed by distillation

The pervaporation membrane can be placed before the distillation column and a saturated liquid feed is fed to the pervaporation membrane. The pervaporation membrane is used to reduce the concentration of methanol so as to get MTBE of good purity in the bottom of the column. The output from the pervaporation unit i.e. the retentate, is then fed to the distillation column so as to get the MTBE of high purity in the bottoms of the distillation column. The area of the pervaporation membrane is the main governing factor in this process. The simulations were run for the different areas and it was found that the area of 1600 m² was suitable for getting MTBE purity of almost 98% in the bottoms of the distillation column. This option is also economical from the heat economy point of view since a saturated liquid feed is fed to the pervaporation membrane, where the concentration of methanol is reduced to some extent and then the

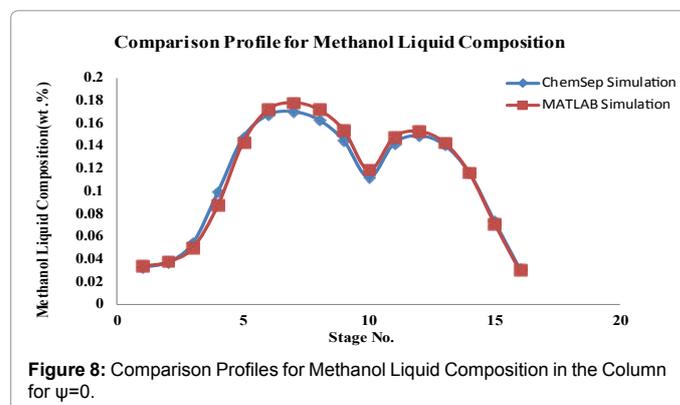


Figure 8: Comparison Profiles for Methanol Liquid Composition in the Column for $\psi=0$.

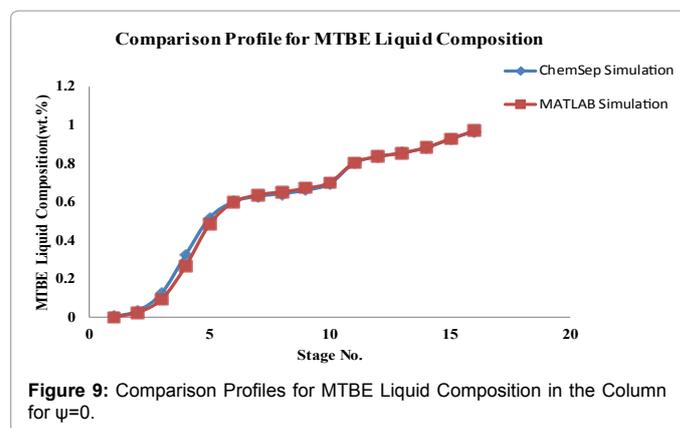


Figure 9: Comparison Profiles for MTBE Liquid Composition in the Column for $\psi=0$.

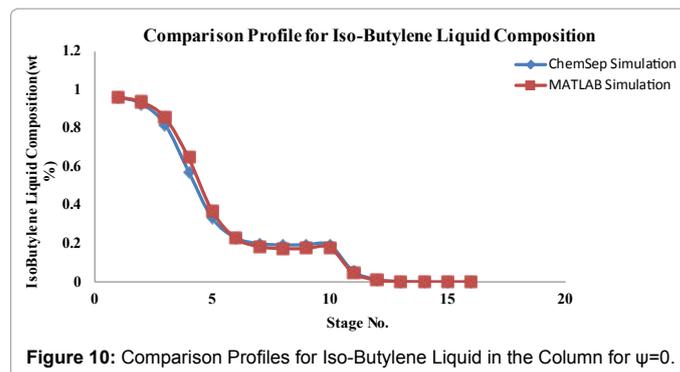
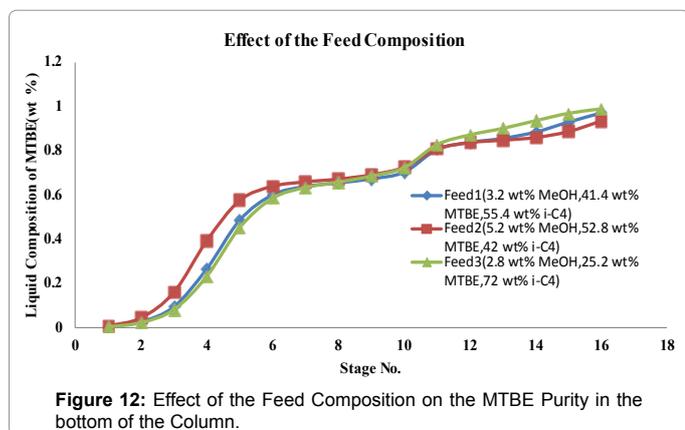
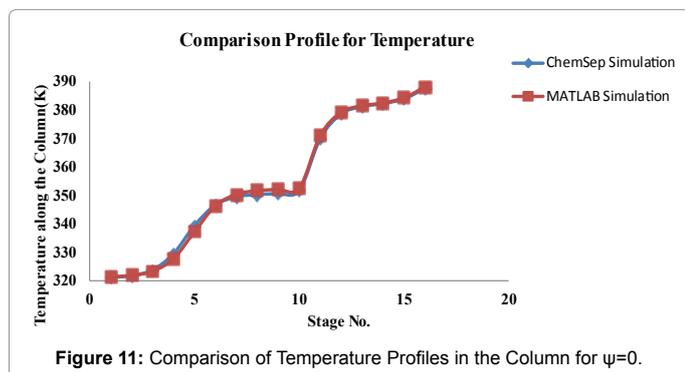


Figure 10: Comparison Profiles for Iso-Butylene Liquid in the Column for $\psi=0$.



retentate from the pervaporation membrane is fed to the distillation column so as to get the MTBE of high purity.

Figure 13 shows the comparison of methanol liquid composition profiles for the distillation and the hybrid process (pervaporation+distillation) with pervaporation followed by distillation. It can be depicted from this graph that methanol peak concentrations are reduced to some extent when a saturated liquid feed is first fed to the pervaporation unit. It is obvious, because most of the methanol permeates through the membrane that causes the reduction in the methanol peak concentration in the distillation column (Figures 12-15).

Figure 14 shows the comparison of MTBE liquid composition profiles for the distillation process and in the hybrid process (pervaporation+distillation) with pervaporation followed by distillation. It can

be observed from this figure that the concentration of MTBE increases from the top to the bottom of the column in both the cases, but the trend of increase is different in both the cases. In case of the hybrid process (pervaporation+distillation), it can be observed that there is almost negligible composition of MTBE in the first few stages of the column and it starts increasing from the 6th stage up to the 10th stage and at the 10th stage it shows a sudden rise which is because of the feed entering at this stage and then it

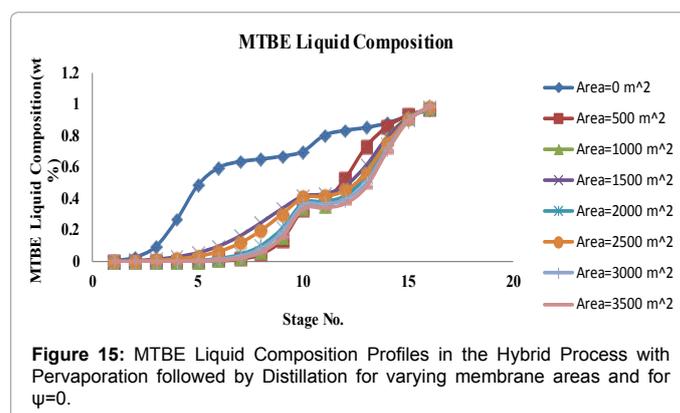
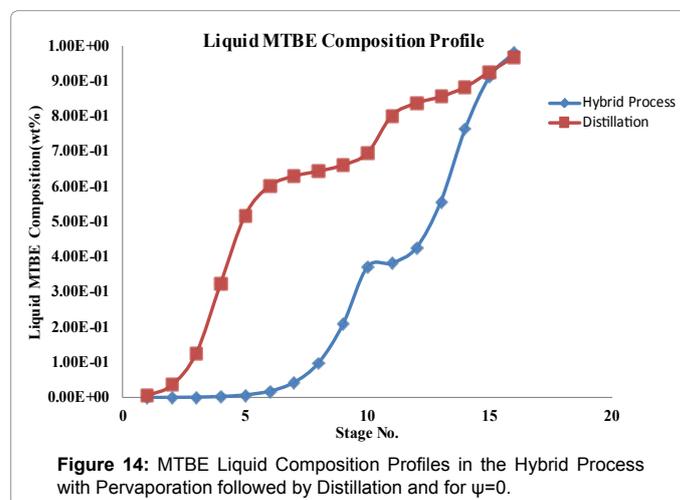
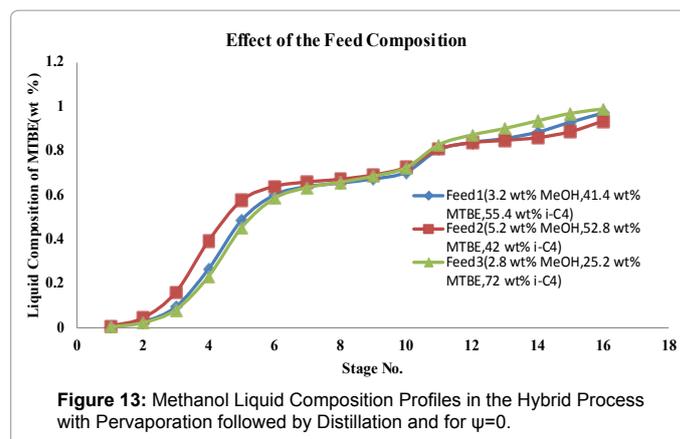
increases upto the 16th stage of the column and it is almost 98% purity of MTBE in the bottom of the column which is more than that obtained in the distillation process alone although not that much purity of MTBE as desired.

Figure 15 shows the liquid phase composition of MTBE in the hybrid process (pervaporation+distillation) with pervaporation followed by distillation. It can be observed that the MTBE concentration increases

in the bottom of the column, as the membrane area is increased. As can be clearly observed that very large area (3500 m²) is required to obtain an MTBE purity of 99% in the bottom of the column, which is highly uneconomical as far as the cost of the membrane is concerned. Hence, it can be concluded that the hybrid process (pervaporation+distillation) in which pervaporation is followed by distillation is not an economically viable alternative.

Pervaporation embedded in distillation

This is possible, because methanol accumulates in the column due to the VLE behaviour of the system. This configuration has already been



discussed in section 4.5. In this configuration, the stage of extraction in the distillation column is the one, where a peak in the concentration profile of methanol in the liquid phase is obtained in the column. In this configuration, pressure and temperature of the stream fed to the column have to be optimized. Therefore, a study has been made to establish the thermal condition of the feed that leads to a greater methanol concentration in the liquid phase inside the column.

It has been established from the distillation column simulation results that the maximum concentration of methanol in the distillation column occurs for the saturated liquid feed. Also the peaks in the rectifying and stripping section are obtained at stage 8 and 12 respectively. Therefore, stage 8 has been selected for the side with draw for the pervaporation operation and stage 12 has been selected to feed the retentate from the pervaporation unit back to the distillation column.

To establish the optimum area of membrane, the simulation has been carried out for the saturated liquid feed and a fraction of side with draw as 0.4 and for different membrane area. The results are shown in Figure 16. The simulation result for zero membrane area (distillation column alone) is also shown in the Figure for comparison. It is observed that the methanol concentration reduces tremendously for the hybrid process; however the area of membrane has very less effect on the methanol concentration in the distillation column. Therefore, a minimum membrane area of (1600 m²) has been selected as optimum area from economic point of view.

To establish the optimum liquid side withdrawal (sw) from the distillation column, the simulation has been carried out for the saturated liquid feed and a constant membrane area (1600 m²) and for different liquid side with draw. The results are shown in the Figure 17. The simulation results for (sw=0) are also shown in the figure for comparison. It is observed that the methanol concentration reduces tremendously for the hybrid process; however the decrease in the methanol concentration in the hybrid process is more as the value of (sw) is increased. It is also clear from the figure that the less methanol concentration in the column is obtained corresponding to (sw=0.4). Methanol concentration can further be reduced by selecting the higher values of sw. However, this will lead to the drying up of the stages of the column. A values of sw=0.4 is recommended in the literature. Therefore, an optimum value of (sw=0.4) has been selected.

Figure 18 shows the effect of the thermal condition of the feed on the liquid phase composition of methanol in the distillation column for a constant membrane area (1600 m²), when a liquid side withdraw

(sw=0.4) is taken from the distillation column and fed to the pervaporation unit. It can be clearly observed from the Figure that the liquid composition of methanol is least in the bottom of the distillation column (which is also desirable for maximum purity of MTBE), when a saturated liquid feed is fed to the column and it is a little more for the half vaporized feed and it's concentration is maximum in the bottom of the column, when a saturated vapor feed is fed to the column. Hence, it can be concluded that it is suitable to give a saturated liquid feed to the distillation column, which is economical from the energy point of view and as well as from the separation point of view (Figures 16-21).

Figure 19 shows the effect of the thermal condition of the feed on the liquid phase concentration (composition) of MTBE in the distillation column for a constant membrane area (1600 m²), when a liquid side draw (sw=0.4) is taken from the distillation column and fed to the pervaporation membrane. It is clearly evident from this graph that the liquid composition of MTBE is the highest in the bottoms, when a saturated liquid feed is fed

to the column and it is a little lesser for the half vaporized feed and it is minimum for the saturated vapor feed being fed to the column. Hence, it is economical to give a saturated liquid feed to the column so as to get the maximum purity of MTBE in the bottoms of the column, which is also desirable from the hybrid process (pervaporation+distillation) with pervaporation embedded in distillation.

Effect of membrane area on MTBE purity

The simulation has been run for the different membrane areas to study its effect on MTBE purity in the bottom of the distillation column

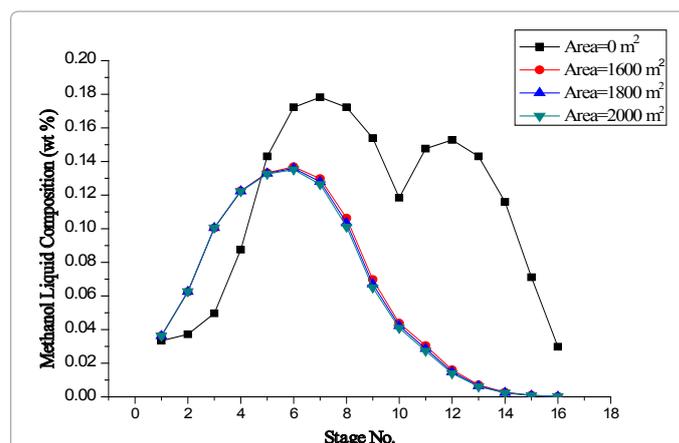


Figure 16: Methanol Liquid Composition Profiles in the Column for varying Pervaporation Membrane Area and for Saturated Liquid feed and sw=0.4.

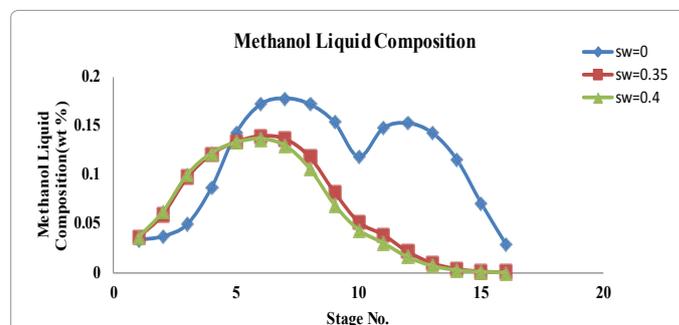


Figure 17: Methanol Liquid Composition Profiles in the Column for varying Liquid Side draws and for Constant Pervaporation Membrane Area and for $\psi=0$.

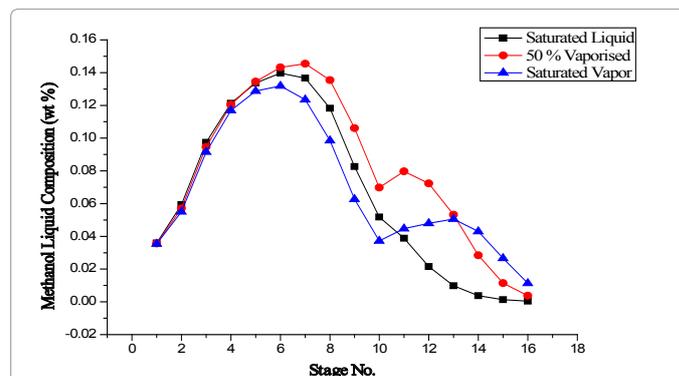


Figure 18: Methanol Liquid Composition Profile in the Column for varying Feed Conditions for the Hybrid Process.

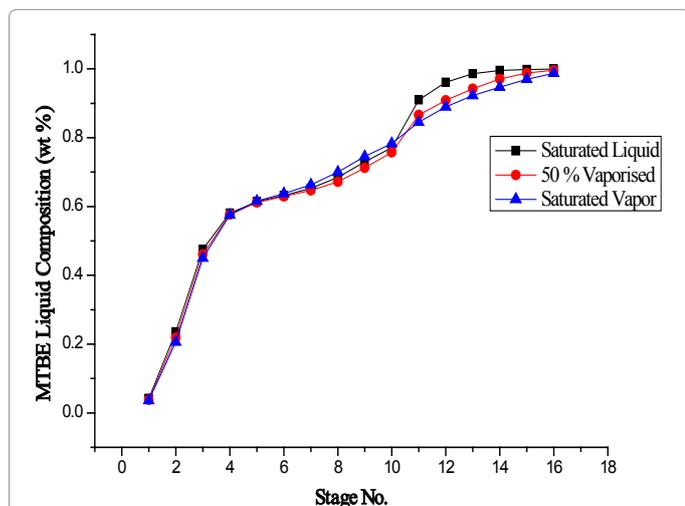


Figure 19: MTBE Liquid Composition Profile in the Column for varying Feed Conditions for the Hybrid Process.

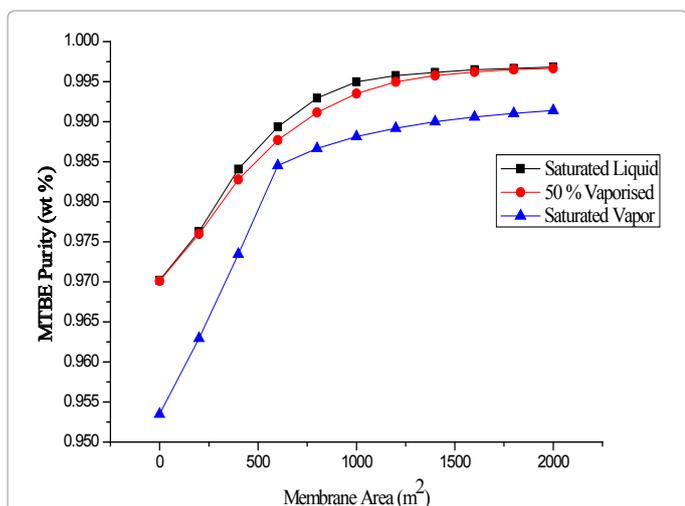


Figure 20: Dependence of MTBE Purity on Membrane Area Requirement for Configuration with Pervaporation Embedded in Distillation for different feed Conditions.

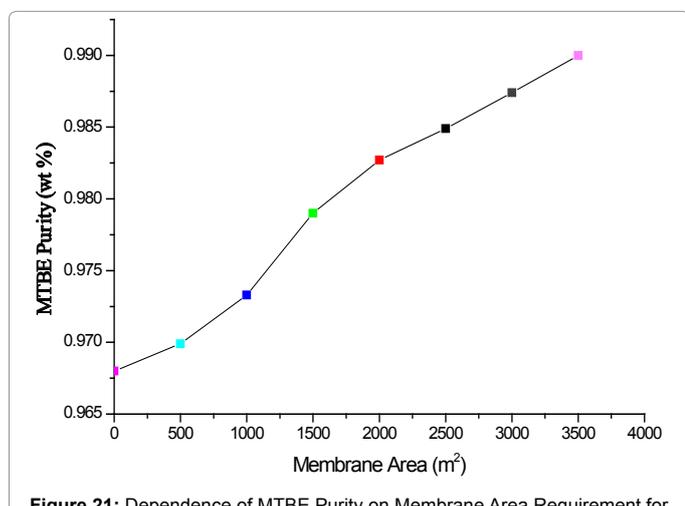


Figure 21: Dependence of MTBE Purity on Membrane Area Requirement for Configuration with Pervaporation followed by Distillation for $\psi=0$.

for the hybrid process, where the pervaporation unit is embedded in the distillation column as described earlier. The results are shown in Figure 20. It is clear from the figure that the MTBE purity increases with the membrane area for all the three thermal conditions of feed (saturated liquid, 50% vaporized and saturated vapor). It can also be observed from the figure that MTBE purity first increases abruptly as the membrane area is increased up to 1600 m² and then it becomes almost constant with further increase in the membrane area for both saturated liquid and 50% vaporized cases. Further, it can be observed from the figure that the MTBE purity obtained with the saturated vapour feed is lower than that obtained with saturated liquid and 50% vaporized feed. It is therefore established that saturated liquid and 50% vaporized feed give the higher MTBE purity. However, saturated liquid feed is considered as the best from the economic point of view. Further, increasing the area beyond 1600 m² causes very small change in the MTBE purity with increased cost of pervaporation unit. Therefore, a membrane area of 1600 m² is considered as optimum which gives about 99.62% MTBE purity in the distillation column.

The simulation has been run for different membrane areas to study its effect on the MTBE purity in the bottoms of the distillation column for the hybrid process, where the pervaporation unit is followed by the distillation column as described earlier. The results are shown in Figure 21. It is clear from the figure that the MTBE purity increases with an increase in the membrane area for saturated liquid feed. It is also observed that a very large area (3500 m²) is needed to obtain an MTBE purity of 99%, which is very high as compared to 1600 m², the area required to obtain the same MTBE purity, when pervaporation unit is embedded in distillation column and therefore is highly uneconomical. It is therefore concluded that, it is better to use the hybrid process, where the pervaporation unit is embedded in distillation column, which is economical both from the MTBE purity viewpoint as well as from the cost-effective viewpoint.

Conclusions

- Equilibrium based, steady-state mathematical model has been developed for the distillation and a separate model has been developed for the pervaporation process (latest membrane separation process). In nutshell, we can say that the hybrid process (pervaporation+distillation) has been modeled.
- Simulations have been carried out for the detailed analysis of the hybrid process (pervaporation+distillation) with respect to the vapor and liquid flow, temperature, and vapor and liquid phase compositions along the stages.
- The combination of distillation and pervaporation helps in achieving products of higher purity as compared to conventional two column scheme.
- As shown in this study, it is possible to obtain MTBE purity of more than 99% for different thermal conditions of feed.
- The mathematical model developed has shown satisfactory results in simulating a hybrid process (pervaporation+distillation) for the separation of MTBE from methanol and iso-butylene.
- The purity of MTBE is maximum in the bottoms of the column, when a saturated liquid feed is fed to the column.
- The purity of MTBE is increased in the bottoms of the column, when a pervaporation membrane unit is connected to the column.
- The purity of MTBE in the bottoms is more in case of the

pervaporation embedded in distillation configurations compared to the pervaporation followed by distillation configuration.

- The pervaporation embedded in distillation configuration requires lesser membrane areas to achieve MTBE purity of more than 99% as compared to the pervaporation followed by distillation configuration, which requires very large membrane area.

Acknowledgment

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