Simulation of Multicomponent Reactive Distilation Column for the Production of Methyl Tertiary Butyl Ether (MTBE)

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Abstract

A multicomponent reactive distillation tray column was simulated. A steady state equilibrium stage model was developed for the production of methyl tertiary butyl ether (MTBE) using Isobutene and methanol in the presence of inert n-butane. The model incorporated reaction kinetics and vapour-liquid idealities into the material and heat balance equations. The matrix equation obtained was solved by successive substitution method. The simulation was done using Microsoft Visual Basic programming. The profiles for the composition and temperature were obtained. MTBE purity level of 63.96 percent obtained from this work has deviations of 3.44 and 1.55 percent from previous works validated the developed model. The temperature profile ranged from 368K at the condenser to 419K at the reboiler. The influence of fresh column feed was investigated and a quadratic increase was ascertained when methanol fresh feed flow rate was varied between 300 – 1000 Kmol/hr. As the feed ratio was varied between 0.99 and 1.30, isobutylene concentration began to decline at 1.13 of the feed ratio input. Multiplicity effect was observed between 2 and 9 when reflux ratio was varied from 1 to 12. Variation of butenes feed temperature from 300 to 400K gave output of 26.66MW to 15.62MW (41.40% difference) reboiler heat duty and methanol feed temperature gave 22.0 MW to 20 MW (7.6%) reboiler heat duty. The model can be applied to design and simulate separation capability of an industrial column for multicomponent reactive distillation.

Keyword: Simulation, Multicomponent Reactive Distilation, MTBE production

1.0 INTRODUCTION

In the current context of cost reduction, environmental protection combined with a significant increase of computational power, chemical engineering equipments based on the integration of several functions in a single apparatus is increasingly been studied. Reactive distillation process (RD) is certainly one of the most significant examples combining reaction and separation in a single apparatus presents numerous advantages from a reaction point of view—improved conversion and selectivity, reduced catalyst requirement, heat integration benefits and avoidance of azeotropes and can be applied in various areas of chemical engineering: esterification reactions [1] hydrolysis of esters [2], etherification [3] and alkylation reactions [4]. The production of MTBE from the reaction of isobutene with methanol in the presence of inert components n-butane [5] and/or 1-butene is an important process because of the characteristics of MTBE as an antiknock agent [6]

In the paper of Jacobs and Krishna [7], it was shown that for an MTBE synthesis column the variation of the methanol feed stage location results in either high or low conversion of isobutene. Explanation of the occurrence of multiple steady states in the MTBE process, using Jacobs- Krishna column configuration, was provided by Higgler *et al.* [8]. However, it is important to point out that investigation of multiple steady states for a chosen system is affected by the selection of an adequate mathematical model and is strongly dependent on the parameters which describe physical properties of real mixtures, reaction kinetic and equilibrium, V–L phase equilibrium, interphase resistance of mass and heat transfers, etc. [9, 10, and 11]. Svandova *et al.* [11] used nonequilibrium model for the simulation of reactive distillation column. They investigated different mass transfer correlations and obtained isobutylene conversion and MTBE purity in reboiler for stable steady states predicted by the models. In another of their work, they compared the performance of reactive distillation column with different hardware configurations. They varied the location of different methanol feed stage. They did not vary the feed flow rate nor did they study the influence of feed ratio to isobutylene conversion. Jacobs and Krishna [7] showed that for MTBE synthesis column, the variation of methanol feed stage location results in either high or low conversion of isobutylene. They did not investigate the variation of methanol feed rate and its impact on MTBE production.

This work developed equilibrium stage model for reactive distillation column and the model was used for the simulation of MTBE production.

The results of MTBE purity was compared to that obtained by Svandova *et al.* [11] for nonequillibrium model and Daza *et al.* [5] reactive distillation column design. Present work investigated the impact of methanol/ isobutylene feed ratios to the performance of the reactive distillation column and also studied the impact of methanol flow rate and feed ratio to reboiler duty. The influence of reflux ratio on MTBE purity was also addressed.

2.0 MODELS

2.1 Overall Stage Model

Figure 1 shows a schematic diagram of trays in a distillation column. It also shows the direction of component i to and from stage j.

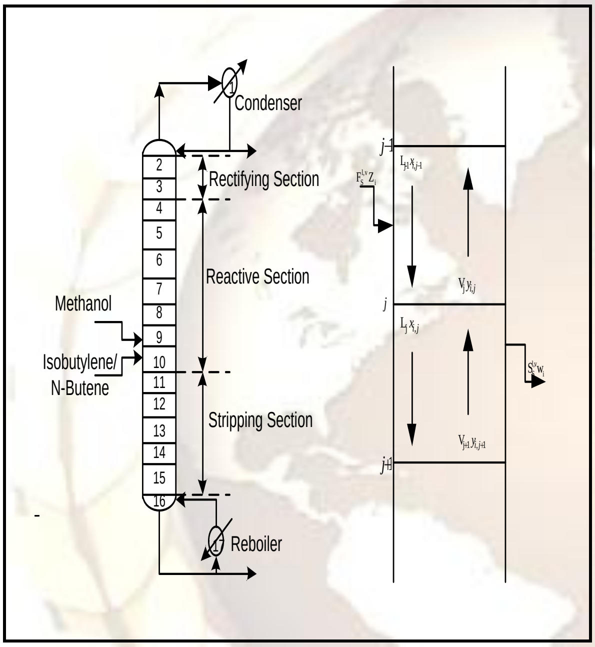

Figure 1: A schematic of Reactive Distillation Column and the Regime for Component i in Tray j

Model Assumptions

In the derivation of the models, the following assumptions are made:

1) A steady state equilibrium condition
2) Feed stream and side stream is channeled to stage j
3) Reaction takes place in stage j
4) Equilibrium distribution coefficients were assumed to be constant for all at all temperatures in each stage of the column.
5) The initial liquid and vapour flow rate, L_j and V_j in each of the stages were assumed constant.
6) Bottom withdrawal flow rate was assumed to be constant.

2.2 Component Balance Equation

Applying the conservative principle to the tray column in Fig. 1 based on the above assumptions, gives the overall component balance in a stage for a reactive distillation as:

$$L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_s^l Z_i^l + F_s^v Z_i^v = L_j x_{i,j} + V_j y_{i,j} + S_s^l W_i^l + S_s^v W_i^v + \Pi_{i,j} \qquad (1)$$

where L, V, F, and B, are the liquid vapour, feed and botoms flow rates respectively, x, y and f are the liquid, vapour, and feed mole fractions respectively

2.3 Energy Balance Equations

Applying the conservative principle to the tray column in Fig. 1 based on the above assumptions, gives the overall energy balance in a stage for a reactive distillation as:

$$H_{j-1}^l + H_{j+1}^v + H_f^l + H_f^v = H_j^l + H_j^v + H_s^l + H_s^v + H_r \qquad (2)$$

The stage liquid and vapour enthalpies are given by

$$H_j^l = \sum_{i=1}^n h_{i\ j}^l l_i \quad and \qquad H_j^v = \sum_{i=1}^n h_{i\ j}^{vl} v_i \qquad (3)$$

where, the liquid and vapour flow rates for specie i in stage j are given as

$$l_i = x_i L_j \quad and \quad v_i = y_i V_j \qquad (4)$$

And $h_{i,j}^i$ and $h_{i,j}^v$ are molar enthalpies of specie i in stage j

2.4 Column Models

Fig. 1 also show the schematic for a hybrid column described by Jacobs and Krishna [7] adopted for the coloum modeling in this work. A hybrid column is one where chemical reactions do not occur throughout the column but in the reactive section only. The column consists of a condenser (in this case a total condenser), a rectifying section (2 trays), a reactive section (8 trays), a stripping section (5 trays) and a reboiler. Reactive section is so because of catalyst in that layer. The column has 15 trays, but 17 stages, the condenser is regarded as a stage and the reboiler is also regarded as a stage. Reaction is assumed to take place only in the reactive section.

Condenser

For a total condenser, the component flow rate is the liquid flow rate to stage 2 and the distillate liquid flow rate. Assume that there is no chemical reaction can be written as

$$V_{j+1}y_{i,j+1} = L_j x_{i,j} + D\,x_{i,D} \qquad (5)$$

where $R = {L_1}/{D}$ and $x_{i,j} = x_{i,D}$

The component balance equation in a total condenser becomes

$$V_{j+1} y_{i,j+1} = D(R+1) x_{i,j} \qquad (6)$$

Rectifying section

In the rectifying section there is neither feed stream nor side stream, assume no chemical reaction, the component balance becomes

$$L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} = L_j x_{i,j} + V_j \, y_{i,j}$$

Reactive section

Chemical reaction occurs in this section. The column configuration did not consider side stream, however there are two feed stream in two out of eight trays in the reactive section. Eq. 1 can be written as

$$\begin{aligned} & L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} + F_s^l Z_i^l + F_s^v Z_i^v \\ & = L_j x_{i,j} + V_j y_{i,j} + \Pi_{i,j} \end{aligned} \qquad (7)$$

Stripping section

In the stripping section there is neither feed stream nor side stream, assume no chemical reaction, the component balance becomes

$$L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} = L_j x_{i,j} + V_j y_{i,j} \quad (8)$$

Reboiler

In the partial reboiler, a liquid flow rate is released from the bottoms and there is no vapour flow into the reboiler. Assume that there is no chemical reaction, eq. 1 becomes

$$L_{j-1} x_{i,j-1} = W_j x_{i,w} + V_j y_{i,j} \qquad (9)$$

2.5 Chemical Reaction and Reaction Term

The chemical reaction for the production of methyl tertiary butyl ether (MTBE) denoted by C, involves the reaction of Isobutylene (IBTE) denoted by A and Methanol (MEOH) denoted by B. Normal butane (NB) goes in with the isobutylene stream and serves as inert. The chemical reaction is reversible and is represented by the equation:

$$A \;+\; B \;\leftrightarrow\; C$$

$\sigma A = -1, \sigma B = -1, \sigma C = 1$ Stoichiometric coefficient

Reaction term

The reaction term is defined as [12]

$$\Pi_{i,j} = \Sigma \sigma r_i \, \varepsilon \qquad (10)$$

where σ is stoichiometric coefficient, ε is volumetric liquid hold up, and r_i is rate of reaction

The summation of reaction term may not be necessary in this case, the rate equation considered the effect of both forward and backward reaction. Multiple reactions are not considered in MTBE reaction. It is assumed that the reaction rate is that of single reaction. The reaction rate equation adopted is a modified Al-Jarallah equation [12], where the effect of catalyst was put into consideration.

$$r_i = K_S K_A \left[\frac{C_A C_B^{0.5} - C_C^{1.5}}{\left(1 + K_A C_A + K_B C_B\right)^{1.5}} \right] \qquad (11)$$

where the rate constant are express as

$$K_S = Exp\left(28.868 - \frac{87900}{RT}\right),$$

$$K_A = Exp\left(-30.795 + \frac{97500}{RT}\right),$$

$$K_B = Exp\left(38.876 - \frac{119000}{RT}\right)$$

C_A = IBTE mol per l; C_B = MEOH mol per l; and C_C = MTBE mol per l;

2.6 Vapour and Liquid Flow Rates for the Rectifying and Stripping Section

The vapour and liquid flowrate in trays of a distillation column is given by the equations [13]; it is assumed that the flow rate is not affected by the chemical reactions.

$$V_{j+1} = \frac{Q_C + D\left(H_D - H_{L1}\right)}{H_{v,j+1} - H_{L1}} \qquad (12)$$

$$L_{j+1} = V_{j+1} - D \qquad (13)$$

for rectifying section, and

$$V_{j+1} = \frac{Q_B + W\left(H_{L,j} - H_W\right)}{H_{v,j+1} - H_{L,j}} \qquad (14)$$

$$L_j = V_{j+1} + W \qquad (15)$$

for stripping section

Condenser heat load (Q_C) and Reboiler heat (Q_B)

The condenser and reboiler heat load are given respectively by [13]:

$$Q_C = D\left[(R+1) H_{V1} - R H_{L0} - H_D\right] \quad (16)$$

and

$$Q_C = D H_D + W H_W + Q_C + Q_L - F H_F \; (17)$$

Assuming there is no heat losses, $Q_L = 0$

Tray Liquid and vapour enthalpies

The vapour and liquid enthalpies in each stage is given by the sum of molar enthalpy of component i in stage j and the component flow rates

$$H_{Lj} = \Sigma_{i=1}^{n} h_{Li,j} \, l_{i,j} \qquad (18)$$

and

$$H_{Vj} = \Sigma_{i=1}^{n} h_{Vi,j} V_{i,j} \qquad (19)$$

The component flow rates in liquid and vapour phases are expressed as

$$l_{ij} = L_j x_{i,j} \quad and \quad V_{ij} = V_j y_{i,j} \qquad (20)$$

The molar enthalpy of component i is expressed as [14]:

$$h_{L_{ij}} h_{V_{i,j}} = \Delta H_{f_i}(T_r) + \int_{T_r}^{T} C_{P_i}(T)dT \qquad (21)$$

The heat of formation, $H_{f_i}(T_r)$, for species is presented in Table 1

The heat capacity is estimated from the expression [15]

$$C_p = A + BT + CT^2 \text{ (liquid)} \quad (22)$$

$$C_p = A + BT + CT^2 + DT^3 \text{(vapour)(23)}$$

The constants, A, B, C, D, in vapour and liquid heat capacity of IBTE, MEOH, MTBE and NBUT (normal butane) is presented in Tables 2 and Table 3 respectively.

Enthalpies of distillates and withdrawn bottoms and feed (H_D, H_W, H_F) are estimated from the expressions

$$H_D = \Sigma_{i=1}^{n} h_{L_{i,D}} D x_{i,D} \qquad (24)$$

$$H_W = \Sigma_{i=1}^{n} h_{L_{i,W}} W x_{i,W} \qquad (25)$$

$$H_F = \Sigma_{i=1}^{n} h_{L_{i,F}} F x_{i,F} \qquad (26)$$

Stage/ Tray Temperatures

Tray enthalpy calculations are functions of tray temperatures derived from Antoine equation [14]:

$$\ln P^{sat} = A - \frac{B}{T+C} \qquad (27)$$

where A, B and C are Antoine constants presented in Table 4.

The bubble point temperature for each stage is given by

$$T = \frac{B_j}{A_j - \ln P_j^{sat}} - C_j \qquad (28)$$

where

$$P_j^{sat} = \frac{P}{\Sigma_i (x_i y_i / \Phi_i)(P_i^{sat} / P_j^{sat})} \qquad (29)$$

The specie j is arbitrary selected specie from the set $\{i\}$. For simplicity, the terms y_i and Φ_i are assumed to be unity for ideal mixtures. The equations (29) is expressed as

$$P_j^{sat} = \frac{P}{\Sigma_i x_i (P_i^{sat} / P_j^{sat})} \qquad (30)$$

Natural log of saturated pressure for species i, P_i^{sat}, is given by

$$\ln P_i^{sat} = A_t - \frac{B_i}{T + C_i} \qquad (31)$$

Initial temperature for each stage of the column is derived from the summation of the product of mole fraction and saturated temperature of pure species

$$T = \Sigma_i x_i T_i^{sat} \qquad (32)$$

The saturated temperature of pure specie is derived from the Antoine equation

$$T_i^{sat} = \frac{B_i}{A_i - \ln P} - C_i \qquad (33)$$

Antoine constants for IBTE, MEOH, MTBE and NBUT were sourced from Lisal *et al.* [16] and presented in Table 4)

Vapour Liquid Equilibrium (VLE) K- Value

The K value for the liquid and vapour phases of ideal mixtures is given by [14]

$$K_i = \frac{y_i}{x_i} \qquad (34)$$

Rewritten equation (3.44) as

$$y_i = K_i x_i \qquad (35)$$

For $i = 1 \, to \, 4$, i is a set 1 to 4, which represents chemical species as follows 1 – Isobutylene, 2 – Methanol, 3 - Methyl tertiary butyl ether, 4 – N Butane

2.7 Mathematical Solution for the Model Equation

Rearranging equation (1), while substituting equation (35) yields

$$\begin{aligned} & L_{j-1} x_{i,j-1} + L_j x_{i,j} - V_j K_{i,j} x_{i,j} \\ & + V_{j+1} K_{i,j+1} x_{i,j+1} = -F_s^l Z_i^l - F_s^v Z_i^v + \Pi_{i,j} \end{aligned} \qquad (36)$$

Removing the side stream terms

The equation (36) can be expressed as

$$A_j x_{i,j-1} + B_j x_{i,j} + C_{i,j} x_{i,j+1} = E_j \qquad (37)$$

where,

$$A_j = L_{j-1} \qquad (38)$$

$$B_j = -(L_j + V_j K_{i,j}) \qquad (39)$$

$$C_j = V_j K_{i,j+1} \qquad (40)$$

$$E_j = -F_s^l Z_i^l - F_s^v Z_i^v + \Pi_{i,j} \qquad (41)$$

For the rectifying and stripping section, the reaction term is removed from the E vector equation. For the reactive distillation column as shown in Figure 1, the liquid phase of the 17 stages including the condenser and reboiler could be represented in a tridiagonal matrix form [17,18] as,

$$\begin{pmatrix} B_1 & C_1 & & & & & & & \\ A_2 & B_2 & C_2 & & & & & & \\ & & & & & & & & \\ & & A_{j-1} & B_{j-1} & C_{j-1} & & & & \\ & & & A_j & B_j & C_j & & & \\ & & & & A_{j+1} & B_{j+1} & C_{j+1} & & \\ & & & & & & & & \\ & & & & & & A_{16} & B_{16} & B_{16} \\ & & & & & & & A_{17} & B_{17} \end{pmatrix} \begin{pmatrix} X_{i,1} \\ X_{i,2} \\ \\ X_{i,j-1} \\ X_{i,j} \\ X_{i,j+1} \\ \\ X_{i,16} \\ X_{i,17} \end{pmatrix} = \begin{pmatrix} E_1 \\ E_2 \\ \\ E_{j-1} \\ E_j \\ E_{j+1} \\ \\ E_{16} \\ E_{17} \end{pmatrix} \quad (42)$$

The matrix equation, is represented in a short form as

$$A_i x_i = f_i(x_i) \quad (43)$$

where'

A_i – represents the tridiagonal matrix for component i

x_i - the composition vector for the ith component

$f_i(x_i)$ - the right hand vector E, which is a function of the composition

The solution to the matrix problem is successive substitution method from the initial guess vector, $x_i^{(0)}$ The successive substitution is represented as follows:

$$A_i x_i^{k+1} = f\left(x_i^k\right) \quad (44)$$

THERMODYNAMIC PARAMETERS

The physical properties of the entire components were obtained from Jacob and Krishna [7], as shown in Table1. The thermodynamic data for the MBTE system such as molar heat of combustion, constants for liquid heat capacity, constants for vapour heat copacity, Antoine constants, were calculated from literatures as shown in Tables 2, 3, 4, and 5.

Table 1: Input Parameters

Parameters	**Values**
Number of stages:	17(Condenser = 1; Reboiler = 17)
Reflux ratio:	7
Bottoms withdrawal flow rate	640 Kmol/Hr
Feed flow rate: Liquid: Vapour:	 770Kmol/Hr, MEOH 1965Kmol/Hr 64% IBTE and 36 % NBUT
Pressure	1110Kpa

Table 2: Molar heat of formation of components [15]

	$\Delta H_{f_i}(298)$
IBTE	-16,903.36
MEOH	-201,601.2
MTBE	-283.700
NBUT	

Table 3: constants for liquid heat capacity [15]

	A	B	C
IBTE	-113.1346	-0.0361507	3.01275 X 10^{-4}
MEOH	74.86274	-0.102315	4.066567 X 10^{-4}
MTBE	162.0418	-0.173412	7.826743 X 10^{-4}
NBUT	103.2326	-9.500675 X 10^{-3}	-2.335311 X 10^{-4}

Table 4: constants for vapour heat capacity [15]

	A	B	C	D
IBTE	6.271	0.3258	-1.720 X 10^{-4}	3.597 X 10^{-8}
MEH	21.13673	7.0843X10^{-2}	2.5860 X 10^{-5}	-2.850 X 10^{-8}
MTBE	4.460	0.5045	-2.470 X 10^{-4}	3.727 X 10^{-8}
NBUT	-4.020	0.3577	-2.0585 X 10^{-4}	4.805 X 10^{-8}

Table 5: Antoine constants [16]

SPECIES	ANTOINE CONSTANTS		
	A	B	C
Isobutylene	9.132635	-2,125.74886	-33.160
Methanol	11.98696	-3,643.31362	-33.434
MTBE	9.2032355	-2,571.58460	-48.406
N-Butane			

Note: Antoine constants for N-butane were not available in the sourced literature; hence the same constants for Isobutylene were used.

2.8 Solution Algorithm

The algorithm for the successive substitution of triadiagonal matrix was represented as:

1. The initial liquid compositions over each plate $(x_{i,j})$ was assumed to be linear between $x_{i,D}$ (stage 1 - condenser) and $x_{i,B}$ (stage 17 - reboiler) and normalized

by dividing $x_{i,j}$ by $\sum x_{i,j}$ i = 1 and 4 are highest at stage 1, while i = 2 and 3 are highest at stage 17, because of their bubble temperatures.

2. Initial stage temperature was determined from Antoine equation, and from the product of initial composition fraction and the calculated saturated temperature (equations 32 and 33).
3. Computations commenced with i = 1 and the elements of the tridiagonal matrix, A_i, B_i and C_i, (equation 42) were then evaluated using all L_j and V_j assumed or calculated.
4. The matrix equation (43) was then solved for $x_{i,j}$ using Thomas algorithm [17], substituting the initial values of $x_{i,j}^{(0)}$ as calculated in step (1) for the constant terms of the matrix (i.e., E-vector or the right-hand side, $f_i(x_i)$ as specified in equation (44).
5. Successive substitution according to equation (44) was continued to apply repetitively until convergence in $x_{i,j}$ was obtained. As a test of convergence, the following criteria was used

$$\sum_{j=1}^{17}\left(x_{i,j}^{(k+1)} - x_{i,j}^{(k)}\right)^2 \le \varepsilon \qquad 45$$

6. When convergence was achieved, steps (3) to (5) were repeated for all the components for i = 2, 3, 4. This was done for all the values of $x_{i,j}$ (for i = 1 to 4 and j = 1 to 17). The values of $x_{i,j}$ was checked and normalized to make $\sum_{i=1}^{4} x_i = 1$
7. Bubble point temperature calculations as specified in equations (28) to (31) were performed based on the converged values of $x_{i,j}$ as obtained in step (5) to estimate the new temperature profile T_j^n over each plate. Methanol was selected as specie j in the determination of temperature profiles.
8. Vapour and liquid flow rates in each stage across the length of the column were evaluated from enthalpy data as specified in equations (12) to (15). However upper and lower limits were specified for the flow rates. This is to avoid negative values of flow rates, which would have affected the components compositions [17].
9. Steps (2) to (7) were repeated with the new estimated temperature profile and similar iterations were continued until convergence in temperature was obtained. As a test of convergence the following testing criteria was used Wang and Henke in Perry et al. [17].

$$\sum_{j=1}^{N}\left(T_j^{(n)} - T_j^{(n-1)}\right)^2 \le \varepsilon_T \qquad 46$$

$$\varepsilon_T = 0.01N$$

Where N is the number of stages

10. The temperature profile and the concentration distribution of all the components along the height of the column were obtained after convergence.

The simulation algorithm was implemented in Microsoft Visual Basic.

3.0 RESULTS AND DISCUSSION

Table 1 shows the comparison between the [11] and [5] model and model prediction for reboiler purity for lower steady states. The results of [11] was 0.6183 and that of [5] was 0.6497 and the model prediction was 0.6396 indicating that the predicted data agree reasonably well with literatures data. The results shows a deviation of 3.44 and 1.55 percents for the [11] and [5] models respectively. It shows from this analysis that the model developed from this work was not much deviated from other works and the model is reliable.

Table 6: Comparison between model prediction and literatures data of MTBE Reboiler Purity for Lower Steady States

Scandova et al	Daza et al	This work	% deviations
0.6183		0.6396	3.44
	0.6497	0.6396	1.55

3.1 Composition Profile

Figure 2 shows the composition of the components along the column height. The graph fits what Mercado described as intermediate steady state. The composition profile for Isobutylene shows a relatively low concentration throughout the height of the column. It highest concentration is found between stages 4 and 11 (the reactive section) and tailed towards stage 1(condenser) and stage 17 (reboiler). The isobutylene was introduced at stage 11, and is used up in the reactions to produce MTBE. Since it is being used up in the reactive section, it concentration in the condenser and rectifying sections are quite minimal. When compared to the concentration of isobutylene concentration in Figure 3, where reactions did not take place, the concentration at the rectifying section and the condenser did not tail off. This was due to the fact that the isobutylene was not used up, but was transferred from the reactive section to the rectifying and stripping sections. Methanol concentration was relatively low in the condenser (Figure 2), increases gradually in stages 2 and 3, and then stages 4 – 11, but began to fall in concentration towards the reboiler. Methanol concentration in the bottoms is 36 percent and 0.07 percent in the distillate product. Mercado [19] described this condition, where there is substantial percentage of methanol in the bottoms stream, as intermediate isobutylene conversion, while [11] classified it as low. This is showing the effect when the forward equilibrium reaction is displaced to the products (left side of the reaction) and the decrease of the MTBE composition in the rectifying zone. In Figure 3, where there is no chemical reaction, the increase concentration down the column from the 4th stage is steep. It is the major product in the bottoms and did not fall in concentration. Since there was no reactions, methanol was not used up. Hence, it was the major component of the stripping section and the reboiler. In Figure 2, methyl tertiary butyl ether, MTBE, maintained an approximately constant profile in the reactive section, and increased in concentration down the column. When the reaction term was disengaged, there was no MTBE found in the column (Figure 3). The purity of MTBE at the reboiler falls at 63.96 percent (Table 6), that is, lower condition. Svandova et al [11] investigated four models and predicted reboiler purity for upper and lower steady state. The models investigated were: Model 1: AICHE [20], Model 2: Chan-Fair [21], Model 3: Chen-Chuang [22] and Model 4: Zuiderweg [23]. The present work used similar parameters applied in Svandova investigation to predict the reboiler purity for lower stable steady state.

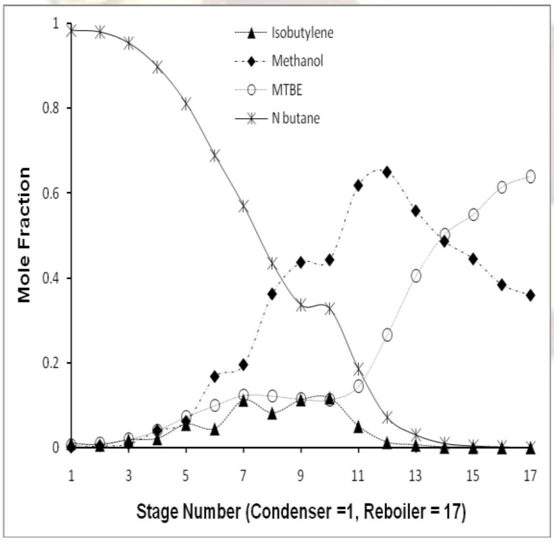

Figure 2: Liquid Phase Concentration Profile for Components (with reaction)

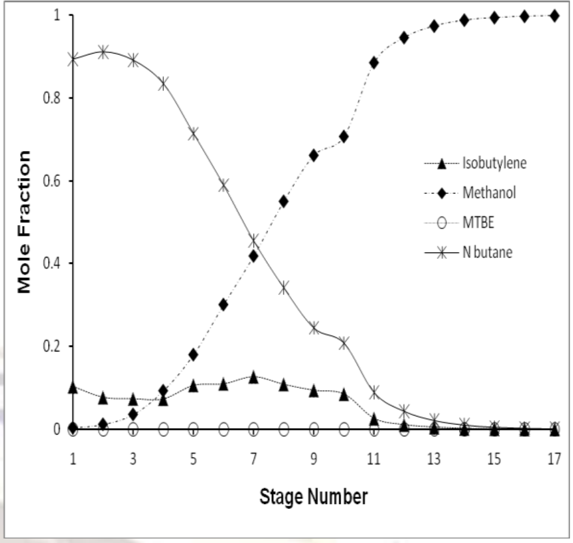

Figure 3: Liquid Phase Composition Profile (without Reaction)

3.2 Temperature Profile

The temperature distribution along the height of the column is depicted in Figure 4. The profile ranged from 368K (at the Condenser) to 419K (at the reboiler). The temperature had a steady rise from the condenser (stage 1) through the stripping section. The effect of chemical reaction and the feed temperature input made the temperature curve to exhibit steady rise from top to bottom of column. It took a steep rise between stage 11 and 12, after which it maintained a steady increase in the stripping section to the reboiler. The effect of reboiler heat could have contributed to the high temperature profile in the stripping section. The column temperature is influenced by the various other factors which include the heat of reactions, the fresh feed rates and the reboiler duty. The temperatures at different feed (methanol/ isobutylene) ratios were plotted in Figure 5. The most affected zones are the reactive and stripping section. Considering feed ratio between 0.85 and 1.27, the temperature increases with increasing feed ratios in the tray. The variation of temperature with methanol flow rate in stages 1 to 3 of the column is depicted in Figure 6. The curves showed multiplicity (multiple steady states) in the condenser and the stripping sections.

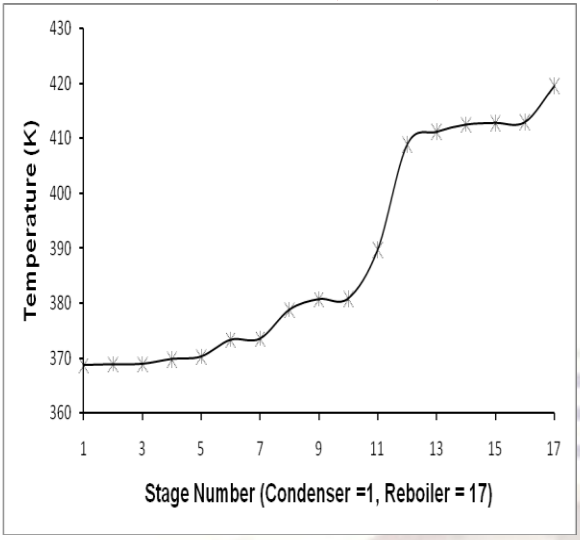

Figure 4: Temperature Profile along the Tray Column

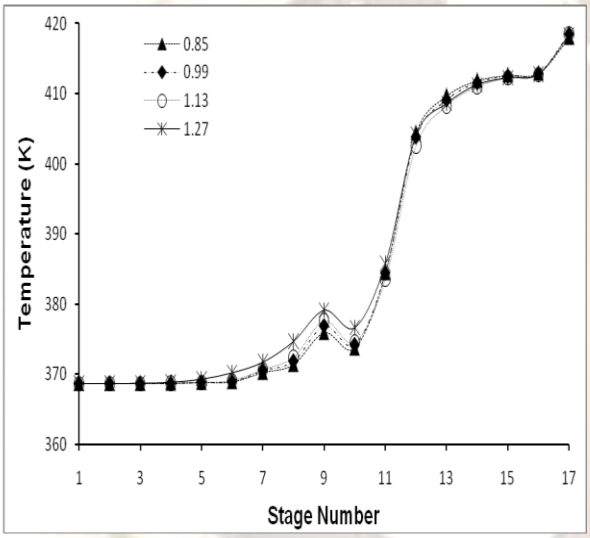

Figure 5: Temperature Profile at Various Feed Ratios

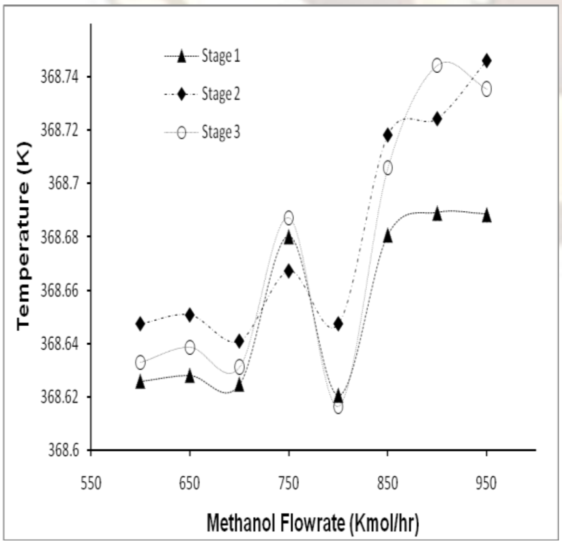

Figure 6: Variation of Stage Temperature with Methanol Flowrate

3.3 Effect of the Variation of Feed Flow Rates

Reboiler Duty

Variation of reboiler duty was done with change in methanol flow rate as shown in Figure 7. The flow rate was varied from 300 to 1000 kmol/hr. The curve relating the flow rate and reboiler duty indicated a quadratic increase of both the dependent and independent variables. The increase in methanol in the feed stream gives more work to the reboiler duty. According to Svandova *et al.* [11], all tray temperatures in the column are very sensible to changes in the reboiler heat duty, especially those of the stripping section. Manipulation of reboiler heat duty immediately change vapour rate in the whole column. They recommended that reaction and separation can be controlled by manipulating the reboiler duty and the feed flow rate.

Isobutylene Concentration

The profile of isobutylene concentration across the height of the column is shown in Figure 8. The feed (methanol/ isobutylene) ratios considered were 0.99, 1.07, 1.19 and 1.30. The two lower feed ratios gave high isobutylene concentrations in each stage. This will favour the forward reaction since Isobutylene is a major driver to the reaction process. Low concentration of Isobutylene in the reactive zone will affect the overall conversion of isobutylene. Figure 9 depicts that isobutylene at the bottoms increased with increase in the feed ratio, which means that the concentration of isobutylene increases due to reverse reaction. In the distillate, isobutylene concentration at 0.011(0.99 feed ratio) begins to reduce at 1.13 feed ratio to 0.005 IBTE (1.30 feed ratio), showing that there was no sufficient isobutylene present for the forward reaction. This phenomenon was explained by Shah *et al.* [12], that the increased methanol rate increases the amount of MTBE carried upward through the stripping section and into the bottom of the reactive section. And this increases the bubble point temperature in the reactive section, promoting the reverse reaction of MTBE to methanol and IBTE and so reducing the equilibrium conversion of IBTE. [12] related feed ratio and isobutylene conversion; there was increase in conversion with increase in feed ratio. The overall maximum conversion was attained at a feed ratio of 1.13.

3.4 Reflux Ratio

The reflux ratio was varied from 1 to 12. The reflux ratio was varied with concentration of MTBE across the height of the column. Figure 10 depicts the curve of MTBE concentration in the reboiler and reflux ratio. At reflux ratio between 2 and 9 the concentration of MTBE exhibit a multiple steady states. Shah *et al.* is of the opinion that because of the multiplicity output from reflux ratio, it is not the best idea to manipulate the reflux ratio to control the flow rate. The reason is that the column response will be too sluggish, since the catalyst weight in the reactive section is too large.

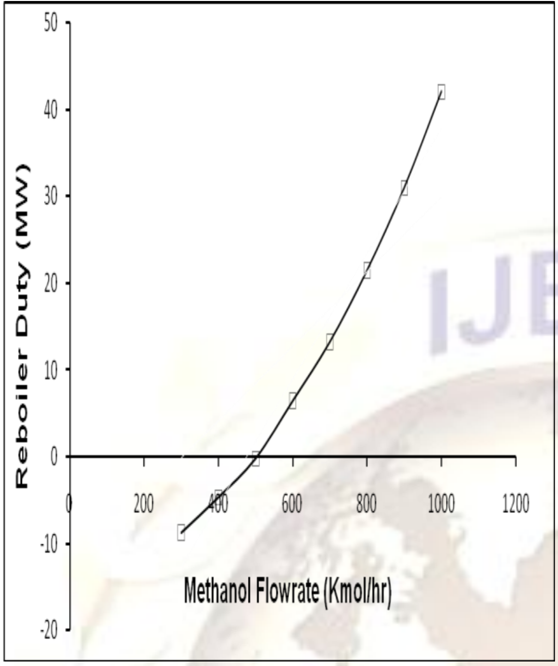

Figure 7: Effect of Methanol Flowrate on Reboiler Duty

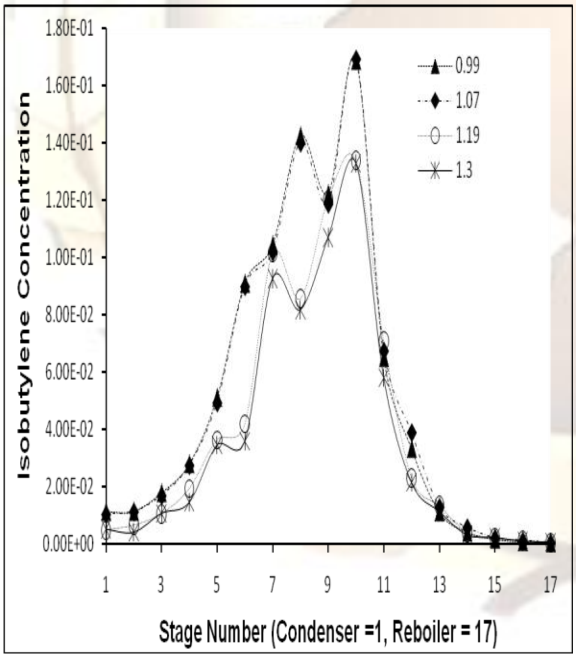

Figure 8: Profile of Isobutylene Concentration at Various Feed Ratio

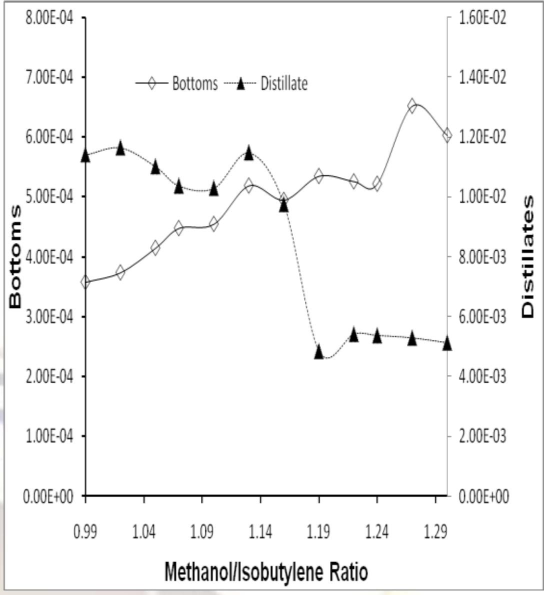

Figure 9: Influence of Feed ratio of Primary Reactants to Isobutylene Composition at bottoms and Distillate

3.5 Feed Temperature

Feed temperature contributes to the overall column temperature and tray stage temperatures. Figure 11 depicts the response of reboiler heat duty to feed temperatures. There are two feed stream in this work and fed to two different trays. For the butenes stream, the reboiler heat duty reduces linearly and steeply with increase in feed temperature. At 300K feed temperature, the reboiler heat duty is 26.66MW, this falls to 15.62MW at 400K (41.40% fall). The heat duty at 300K of methanol feed temperature; the reboiler heat duty is 22.0 MW and had only 7.6 percent fall at 400K.

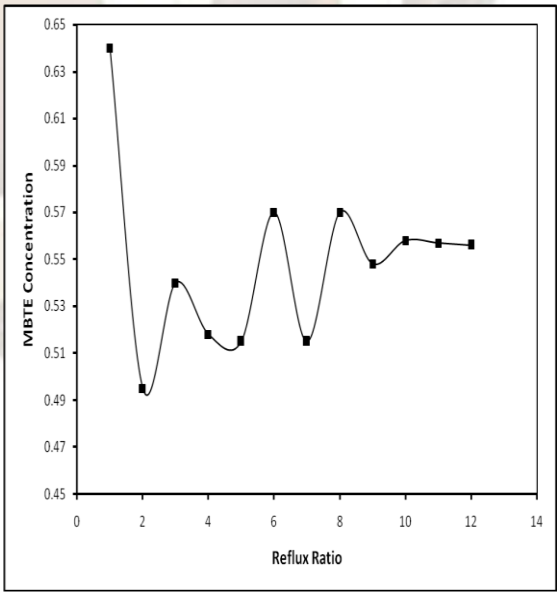

Figure 10: Effect of Reflux Ratio on MTBE Purity

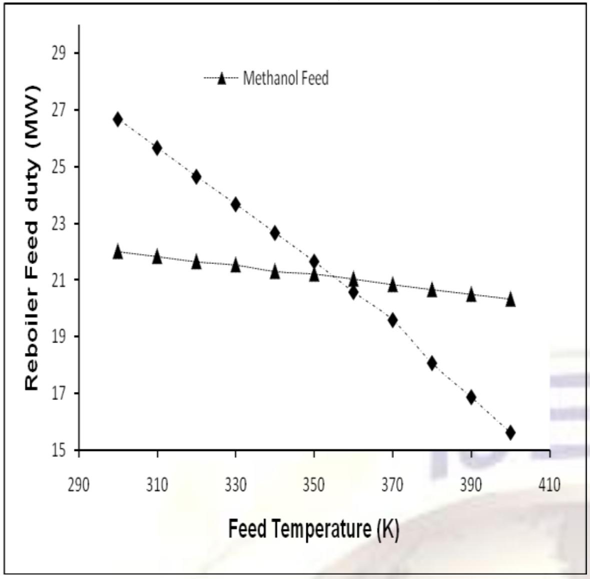

Figure 11: Relationship between Feed Temperature and Reboiler Duty

4.0 Conclusion

The reactive distillation tray column for a multicomponent species was modeled. The model is an equilibrium stage model of Jacob and Krishna (1993) reactive distillation column. The model was simulated using Microsoft Visual Basic programming, for the production of methyl tertiary butyl ether (MTBE). The MTBE production process is a reversible reaction with isobutylene and methanol as reactants and MTBE as the desired product. Other side reactions are not common in this process, but the reverse reaction produce MTBE. This process involves normal butane, which does not react but serves as an inert.

The profile for the composition and temperature were obtained. The composition profile displayed intermediate steady state features described by Mercado [19]. MTBE purity level of 63.96 percent was achieved, which was a deviation of 3.44 percent [11] and 1.55 percent [5] of previous works. The model is thus reliable. The temperature profile ranged from 368K at the condenser to 419K at the reboiler. The feed ratio also had significant effect on the column tray temperatures. The influence of fresh column feed was investigated. A quadratic increase was seen when methanol fresh feed flow rate was varied between 300 and 1000 Kmol/hr. Feed ratio was varied between 0.99 and 1.30, isobutylene concentration began to decline at 1.13 of the feed ratio input. Variation of reflux ratio from 1 to 12 depicted multiplicity effects between 2 and 9. Also the feed temperature was varied with the reboiler heat duty. Butenes feed temperature from 300 to 400K showed a variation of 26.66MW to15.62MW (41.40% difference). And for methanol feed is 22.0 MW to 20 MW (7.6%).

REFERENCES

[1] Bessling, B., Schembecker, G. and Simmrock, K. H.: ‘Design of Processes with Reactive Distillation Line Diagrams, *Industrial and Engineering Chemistry Research*, 36, 1997, 3032.

[2] Gumus, Z. H., and Ciric, A. R. Reactive Distillation Column Design with Vapor/Liquid/Liquid Equilibria, *Computers and chemical Engineering*, 21 1997, S983.

[3] Sundmacher, K.; Homann, U.: Steady state multiplicities in reactive distillation columns for the production of fuel ethers MTBE and TAME: theoretical analysis and experimental verification”, *Chemical Engineering Science*, 54, 1999,1029

[4] Jones E.M. Contact structure for use in catalytic distillation”, *US Patent 4,536,373*, 1985

[5] Daza, O.S. and Perez-Cisneros, E.S: “Graphical and Stage-to-Stage Methods for Reactive Distillation Column Design”, *American Institute of Chemical Engineering Journal* Vol. 49, (11), 2003, 2822

[6] Smith, L. A., and Huddleston, M. N.: ‘‘New MTBE Design Now Commercial,’’ *Hydrocarbon Process.*, 3, 1982, 121

[7] Jacobs, R., and Krishna, R. Multiple Solutions in Reactive Distillation for Methyl Tert-Butyl Ether Synthesis, *Industrial Engineering Chemistry Research* 32, 1993, 1706

[8] Higler, A., Taylor, R. and Krishna, R. Modeling of a reactive separation process using a nonequilibrium stage model, *Computers and Chemical Engineering*, 22,1998, S111-S118

[9] Baur, R., Higler, A. P., Taylor, R. and Krishna, R. Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation,” *Chemical Engineering Journal*, 33(47), 2000, 76

[10] Noeres, C., E.Y. Kenig, Gorak, A. “Modelling of reactive separation processes: reactive absorption and reactive distillation,” *Chemical Engineering Process*, 42(3), 2003, 157–178

[11] Svandova, Z, Markos J. and Jelemensky, L. Impact of mass transfer coefficient correlations on prediction of reactive distillation column behavior, *Chemical Engineering Journal* 140, 2008, 381–390

[12] Shah V., Bluck D., Kovach J., Parikh R., Yu R. and Miller D. Reactive Distillation Configuration, *Simulation sciences Inc.* 1998

[13] Treybal, R. E. *Mass Transfer Operations*, 3rd Ed. McGraw-Hill, Singapore, 1981

[14] Smith, J.M., Van Ness H.C. and Abbott, M.M. *Introduction to Chemical Engineering Thermodynamics, Chemical Engineering Series*, 5th edition: McGraw-Hill companies, New York, 2005.

[15] Himmelblau, D. M. *Basic Principles and Calculations in Chemical Engineering*, 6th Ed. Prentice Hall, Engle Wood Cliff, N.J. PTR, Compact Disc Data, 1996.

[16] Lisal, M., smith, W.R. and Nezbeda, I "Accurate Computer Simulation of Phase equilibrium for Complex Fluid Mixtures - Application to Binaries Involving Isobutene, Methanol, Methyl Tertiary Butyl Ether and n-Butane," *Journal of Physical Chemistry. B*, 103,1999, 10496

[17] Perry, R.H., Green, D.W., Maloney, J.A. *Perry's Chemical Engineers' Handbook*, 7th Edition, McGraw-Hill, New York, 1997

[18] Monroy, R., Perez-Cisneros, E. S. and Alvarez, J. A Robust PI Control Configuration for a High-Purity Ethylene Glycol Reactive Distillation Column, *Chemical Engineering Science*, 55, 2000, 4925

[19] Mercado G.J.R. (2008): *Design and Analysis in Modeling Reactive Separation Processes, PhD. Thesis, University Of Puerto Rico*, 2008

[20] American Institute of Chemical Engineering: *AICHE Bubble Tray Design Manual*, New York, 1958.

[21] Chan, H., and Fair, J.R. "Prediction of point efficiencies on sieve trays, 1: Binary systems," *Industrial and Engineering Chemistry Research* 23(4),1984, 814–819.

[22] Chen, G.X., and Chuang, K.T. Prediction of point efficiency for sieve trays in distillation, Industrial *and Engineering Chemistry Research* 32, 1993 701–708

[23] Zuiderweg, F.J. Sieve trays: a view on the state of the art," *Chemical Engineering Science* 37(10), 1992, 1441–1464.

Nomenclature

C_p	heat capacity (KJ/Kmol.K)
D	distillate flow rate (Kmol/Hr)
F	Feed flow rate (Kmol/Hr)
h	molar enthalpy (KJ/Kmol)
H	enthalpy rate (KJ/Hr)
L	liquid flow rate (Kmol/Hr)
P	pressure (KPa)
Q	heat loss or gain (KJ/Hr)
r	reaction rate (Kmol/m^{3}Hr)
R	reflux ratio
S	Side stream flow rate (Kmol/Hr)
T	temperature (K)
V	vapour flow rate (Kmol/Hr)
w	side stream mole fraction
W	bottoms withdrawal rate (Kmol/Hr)
x	liquid mole fraction
y	vapour mole fraction
z	liquid mole fraction in feed

Greek symbols

ε	liquid hold up (Kmol)
γ	activity coefficient
Φ	fugacity coefficient
σ	stoichiometric coefficient

Subscripts

B	reboiler
C	condenser
D	distillate
f	feed
i	component
j	tray
L	liquid
r	reaction
s	side stream
V	vapour
W	bottoms withdraw

superscripts

l,v	liquid, vapour
s	stream, use for feed and side stream