Modeling Reactive Distillation for Tertiary Ether Synthesis

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Abstract

Reactive distillation has enormous potential for the economical synthesis of tertiary ethers, which are good octane boosters. Methyl tert-butyl ether (MTBE) has been commercially produced with this technology since the early 1980s and it appears that the process also has application for Ethyl tert-butyl ether (ETBE) and other ethers.

In the present work, an equilibrium based steady state model of a reactive distillation column for the synthesis of ETBE, has been developed. The model equations were solved using data given in the literature by using MATLAB software. The results thus obtained have been compared with the published results and were found in good agreement.

Liquid and vapor flow rate at each stage, temperature profile and composition profile along the stage were plotted. The result shows a sharp change near the feed stage, in the flow profiles. The similar pattern was seen in temperature profile. In the composition profile, there is a sharp increase in the composition of water at feed stage as feed stream contains 95% water. The result has been discussed in detail.

Keywords: reactive distillation, ethyl *tert*-butyl ether, modeling, simulation, steady state,

1. INTRODUCTION

Reactive distillation (RD) is one major step in the history of distillation in improving its performance. RD processes couple chemical reactions and physical separations into a single unit operation which not only reduces the overall capital cost of a process but also provides process benefits in some cases. An added benefit is the increased energy efficiency which results from direct utilization of heat of reaction for fractionation. These processes, as a whole are not a new concept as the first patent dates back to the 1920s. It can be utilized for both equilibrium and non-equilibrium reactions.

As lead compounds in the fuels are threat to public health and for environment, oxygenates are gaining importance as a gasoline blend components. They serve not only as gasoline extenders and as octane boosters but also as a key ingredients for reducing the emission of CO and VOCs

The two main classes of competing oxygenates at present are alcohols and ethers. In general however ethers are preferred over alcohols because of their fungibility, less polar character and high individual vapor pressure.

The predominant oxygenate used at present is methyl *tert*-butyl ether (MTBE) synthesized commercially by the exothermic liquid phase reaction of methanol and isobutylene over an acid ion-exchange resin catalyst. As the price of methanol goes up in relation to gasoline, ethyl *tert*-butyl ether (ETBE) becomes more attractive relative to MTBE. ETBE is produced from renewable ethanol, thus help mitigate the green house effect. Also, it outranks MTBE as an octane enhancer. Furthermore, ETBE has a lower oxygen content (15.7 wt %) than does MTBE (18.2 wt %) and ethanol (34.70 wt %). In this manner, ETBE blends allow the greatest reduction in concentration of aromatics, sulfur and benzene, which is an objective to be reached in clean gasoline. Groundwater contamination associated with MTBE has also forced refiners all over the world to find a viable alternative.

2. KINETICS

The simulation of reactive distillation requires kinetics that express the rate of reaction. The following reversible reactions may take place in the synthesis of ETBE from TBA and EtOH

$$\text{EtOH} + \text{TBA} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{ETBE} + \text{H}_2\text{O} \qquad (1)$$

$$\text{TBA} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{IB} + \text{H}_2\text{O} \qquad (2)$$

$$\text{IB} + \text{EtOH} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \text{ETBE} \qquad (3)$$

since the solubility of IB in the liquid mixture is low under atmospheric conditions, reaction (3) is negligible [1].Using Potassium Hydrogen Sulfate ($KHSO_4$) selectivity is the highest than other catalyst [2]. As a result, only reaction (1) is considered. The rate laws of the reaction and the rate constant expressions are taken as given by Assabumrungrat et al. [3].

3. MODEL EQUATION FOR REACTIVE DISTILLATION.

The RD was modeled using sixteen equilibrium stages including a partial condenser and a partial reboiler, like the work of Quitain et al.[1]. The specifications are given in Table 1.The model equations for a generic stage j and component i are represented based on the commonly used distillation equations, with incorporation of the reaction terms (Figure 1):

The total material balance on stage j is given by:

$$L_{j-1} + V_{j+1} + F_j - V_j - S_j^v - L_j - S_j^l + m_j \sum_{i=1}^{c} \sum_{k=1}^{r} \upsilon_{i,k} r_{k,j} = 0 \qquad (5)$$

The last term $m_j \sum_{i=1}^{c} \sum_{k=1}^{r} \upsilon_{i,k} r_{k,j}$ is the rate of disappearance of the total moles due to any k reaction on stage j. The material balance for component i on stage j is given by:

$$l_{j-1,i} + v_{j+1,i} + f_{j,i} - v_{j,i} - s_{j,i}^l - l_{j,i} - s_{j,i}^v + m_j \sum_{k=1}^{r} \upsilon_{i,k} r_{k,j} = 0 \qquad (6)$$

Where $\qquad\qquad l_{j,i} = L_j x_{j,i} \quad \& \quad v_{j,i} = V_j y_{j,i} \qquad\qquad (7)$

The compositions of the streams leaving a stage are in thermodynamic equilibrium. Therefore

$$y_{j,i} = K_{j,i} x_{j,i} \qquad (8)$$

Defining $A_{j,i} = L_j / K_{j,i} \times V_j$, equation (8) is reduced to

$$l_{ji} = A_{j,i} v_{j,i} \qquad (9)$$

Summation equations in terms of flow rate of components are

$$\sum_{i=1}^{c} l_{j,i} = L_j \qquad\qquad \sum_{i=1}^{c} v_{j,i} = V_j \qquad (10)$$

The energy balance for stage j is:

$$L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V + F_j H_j^F - (V_j + S_j^v) H_j^V - (L_j + S_j^L) H_j^L - Q_j = 0 \qquad (11)$$

Since enthalpies are referred to their elemental state, no heat of reaction term explicitly appears in the energy balance because it is automatically accounted for.

The following assumptions are made in formulating the reactive distillation process for ETBE synthesis:
1) The vapor and liquid leaving each stage are in equilibrium.
2) The reaction only occurs in liquid phase.
3) Each stage in reaction section is considered as a CSTR reactor.
4) The heat loss and mass transfer resistance are neglected.

4. SIMULATION PROCEDURE.

In order to predict the performance of the model, solution of the model is essential. The developed model equations are solved by following procedure [4]:
1) An initial set of values for T_j and L_j/V_j are assumed.
2) Absorption factor (A_{ji}) is calculated.
3) Component balances for all the four components are solved simultaneously for l_{ji}.
4) The θ method of convergence is used to find corrected set of composition which was in turn used to find a new set of temperature.
6) A new set of total flow rates are calculated.
7) The above procedure is repeated until convergence criteria have been satisfied.

5. RESULTS AND DISCUSSION.

The equations have been solved in MATLAB environment using inbuilt MATLAB routines for solution of nonlinear simulation equations. The column input and specifications are given in Table 1.

Figure 2 show the temperature variation along the stages of the column. The trend is obvious as it shows the lower temperature at the top of the column and higher temperature at the bottom. The temperature at the top, which is also the temperature of the distillate, is corresponding to its bubble point. While the temperature at the bottom stage, is corresponding to the bubble point of the bottom product. Since the bottom contains mostly water, it temperature is nearly the boiling point of water at the stage pressure. The temperature in the striping section shows an increasing trend because more and more low boiling components are stripped off in this section. The reactive zone also exhibits the similar trend. This is because of more production of ETBE in the lower section of the zone. Since the ETBE synthesis reaction is exothermic, this causes an increase in temperature for higher production rate of ETBE. The temperature in the rectifying section is almost constant as the low boiling components are vaporized in the lower section of the column causing very less separation of components in this section. This causes the negligible variation of temperature in this section

Figure 3 shows the liquid and vapor flow at each stage. Both figures show an increase in the flow rate near the feed stage. When the feed enters the feed stage where it is flashed at the stage temperature and pressure, the part of the feed is vaporized and the remaining will be liquid. The liquid part will flow in stripping section, thus increasing the liquid flow rate in this section. The increase in vapor flow in stripping section is because, the temperature in the feed stage and striping section which is near the boiling point of water. The vapor produced in this section will also be large due to evaporation of water from the feed which caused an increased flow rate in the striping section.

Figure 4 shows the variation of the liquid composition of various components at each stage. It shows almost negligible compositions of ethanol, TBA and ETBE in the stripping section which is obvious as they are low boiling components in comparison to water and are essentially stripped off in this section, leaving only water whose concentration is as high as 97% at the bottom stage. The variation of composition in the rectifying section is almost constant because of the reasons mentioned earlier. The decrease in the composition of ethanol and TBA in reactive section is because of their consumption in this section and for the same reason the water composition increases in this section. ETBE composition in the rectifying section is very low. This may be due to higher composition of water in the feed which causes the backward reaction rate to be high thus most of the ETBE produced is disappeared.

Figure 5 shows the variation of vapor phase composition along the column. The negligible composition of ETBE is justified because of the higher rate of backward reaction which occurs in liquid phase. A decrease in the composition of ethanol and TBA in the reactive section is due to same reason as described for the liquid phase composition. The stripping section also follow the similar trend as those of liquid phase composition because of the similar reasons.

The simulation results presented in this work have been compared with the results of Quitain et al. [1].The results for the bottom product are in good agreement with the published result. However, there is variation in the result for the distillate. The reason for this variation might be because of the assumption that no side reaction takes places in presence of the catalyst KHSO$_4$ (Matouq et al. [2]), which is also considered in the present work.

6. CONCLUSION

It may be concluded that the developed model is suitable for studying the behavior of the column under prevailing operating conditions. Equilibrium based, steady state mathematical model, for synthesis of ETBE using Reactive Distillation column has been developed. The model equations are solved by using MATLAB 6.5 software.

Simulation has been carried out for the detailed analysis of Reactive distillation column with respect to the vapour and liquid flow, temperature, and vapour and liquid compositions along the stages. The results obtained have been compared with those of Quitain et al. [1] and were found in good agreement for the bottom products. A slight variation in the results for distillation was because of the assumption of no side reaction in the present work.

NOMENCLATURE

Notations

A_{ji}	Absorption factor for component i on jth stage.
c_i	Concentration of component i.
D	Total molar flow rate of distillate.
d_i	Molar flow rate of component i in the distillate.

F	Molar flow rate of the feed.
f_{ji}	Molar flow rate of component i in the feed stream leaving jth stage.
H	Molar Enthalpy of stream
h_{ji}	Partial molar enthalpy of component i in the liquid phase leaving jth stage.

H_{ji}	Partial molar enthalpy of component i in the vapour phase leaving jth stage.		T_j	Temperature at jth stage.
k	Rate constant.		V_j	Total Molar flow rate at which vapour phase leaves jth stage.
K_{ji}	Equilibrium vapourization constant; evaluated at the temperature and pressure of liquid leaving jth stage.		v_{ji}	Molar flow rate of component i in the vapour phase leaving jth stage.
L_j	Total Molar flow rate at which liquid phase leaves jth stage.		x_{ji}	Mole fraction of component i in the liquid phase leaving jth stage.
l_{ji}	Molar flow rate of component i in the liquid phase leaving jth stage.		y_{ji}	Mole fraction of component i in the vapour phase leaving jth stage.
m	Mass of catalyst.			

Superscripts

L	Liquid phase
V	Vapour phase

Q_j	Heat duty.
Q_c	Condenser duty.
Q_R	Reboiler duty.

Subscripts

i	Component number.
j	Stage number.
k	Counting number.

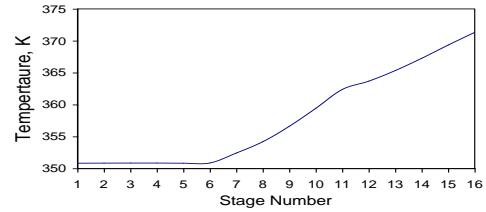|	
r	Rate of reaction of the base component.
R	Gas constant
S	Molar flow rate of the side stream.
s_{ji}	Molar flow rate of component i in the side stream leaving jth stage.

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240

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http://www.ijmra.us   **Page** 240

Table 1 Reactive Distillation Column Simulation Input [1]

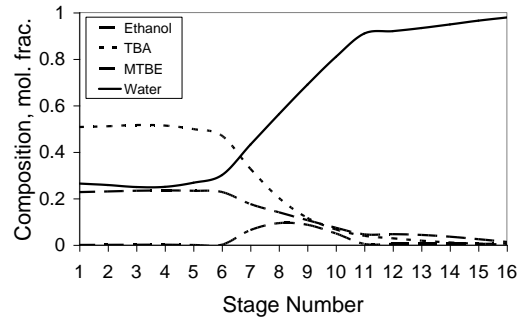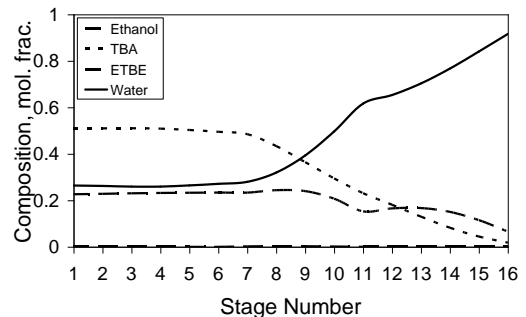| FEED CONDITION	
Feed stage	11
Pressure	101.3 kpa
Temp	298K
Flow rate	4.14 mol/s
Molar ratio	EtOH:TBA:H_2O::1:1:38
Composition [mole%]	
EtOH	2.5
TBA	2.5
H_2O	95
COLUMN SPECIFICATIONS	
Rectification stage	1 to 6
Reaction stage	7 to 10
Stripping stage	11 to 16
Total stages	16
Condenser	Stage 1
Reboiler	Stage 16
Catalyst weight /stage	25 kg
Pressure	101.3 kpa
Reflux Ratio	3.37
Ratio of distillate to feed	.033
Condenser Type	Total
Reboiler Type	Partial

Figure 2 Variation of Temperature along Stage
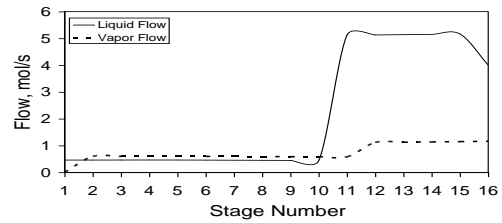
Fifure 3 Variation of Liquid and Vpor Flow along Stage

Figure 4 Variation of Liquid Phase Composition along Stages

Figure 1. General Equilibrium Stage Model, Including Feed Stage and Side Stream Product Withdrawal**.**

Figure 5 Variation of Vapor Phase Composition along Stages

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