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Simulation Studies on Reactive Distillation for Synthesis of *tert*-Amyl Ethyl Ether

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Abstract−In this work, a reactive distillation column in which chemical reactions and separations occur simultaneously is applied for the synthesis of *tert*-amyl ethyl ether (TAEE) from ethanol (EtOH) and *tert*-amyl alcohol (TAA). A rate-based kinetic model for liquid-phase etherification and an equilibrium stage model for separation are employed to study the reactive distillation. The calculation is carried out using the commercial software package, Aspen Plus. Simulations are performed to examine the effects of design variables, i.e., a number of rectifying, reaction and stripping stages on the performance of reactive distillation column. It has been found that an optimal column configuration for the TAEE production under the study is designed with no rectifying, 4 reaction and 8 stripping stages. With such an appropriate specification of the reactive distillation column, the effects of various operating variables on the TAA conversion and TAEE selectivity are further investigated and the results have shown that the reflux ratio and operating pressure are the most important factors to the operation of the reactive distillation.

Key words: *tert*-Amyl Ethyl Ether, Reactive Distillation, Simulation

INTRODUCTION

Reactive distillation, sometimes called “catalytic distillation”, has drawn considerable attention from both academic and industrial sectors over the past decades. Reactive distillation combines a catalytic reactor and a distillation in one single unit operation. Its four potential benefits are: (i) shifting an equilibrium conversion, (ii) reacting away azeotropic mixtures, (iii) improving selectivity and (iv) saving energy due to the efficient use of reaction heat for separation [Baur et al., 2000]. It has been applied to many esterification and hydrolysis processes involving alkyl acetate and glycols, alkylation for cumene, and the formation of fuel oxygenates in chemical and petrochemical industries.

A number of publications dealing with a production of oxygenates in reactive distillation have been published in the past decades. Most of the early works focused on the synthesis of small tertiary ethers (i.e., methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE)) [Hommerich and Rautenbach, 1998; Tang et al., 2003; Assabumrungrat et al., 2004]. However, since it has been reported that MTBE may pollute underground water [Dai, 2000], the production of higher tertiary ethers such as tertiary-amyl methyl ether (TAME) and tertiary-amyl ethyl ether (TAEE) have been of present interest to replace MTBE [Thiel et al., 1997; Kitchaiya and Datta, 1995]. TAEE is a more favorable choice compared to TAME in environmental terms as ethanol, one of the reactants, can be derived renewably from agricultural products such as sugar cane, corn and potatoes. Most previous works considered the production of TAEE from isoamylene (IA) and ethanol in reactive distillation [Kitchaiya and Datta, 1995; Linnekoski et al., 1997]. Tertiary amyl alcohol (TAA), a main component in fusel oil which is a byproduct from the fermentation process for the ethanol production, can be an alternative reactant instead of IA. Therefore, the synthesis of TAEE from TAA and ethanol should be a promising route as both reactants are derived from renewable resources [Chang et al., 1998].

Unfortunately, there are still very limited efforts concerning this reaction system. Only one work is found in the literature considering the synthesis of TAEE via this route in a reactive distillation [Aiouache and Goto, 2003b]. It is, therefore, the aim of this study to investigate in more detail the performance of reactive distillation for the production of TAEE from TAA and ethanol. Simulation studies are carried out using the ASPEN PLUS simulator. Emphasis is placed on the determination of an appropriate configuration of the reactive distillation column for the TAEE production. In addition, an analysis of the effects of key operating parameters such as reflux ratio, operating pressure, and feed stage location, on the conversion of TAA and the selectivity of TAEE is performed.

STUDIES ON THE SYNTHESIS OF TAEE IN REACTIVE DISTILLATION

1. Reactive Distillation Model

Simulation of the synthesis of TAEE in a reactive distillation (RD) is carried out by using the Aspen Plus simulation package. The RADFRAC model, which is a rigorous equilibrium-stage distillation model to describe a multistage vapor-liquid separation in the distillation column, is used in this study. The equilibrium stage model is often applied with great success for the simulation of distillation columns [Dirk-Faitakis and Chuang, 2003]. Similar to our previous work [Assabumrungrat et al., 2004], the property option set PSRK

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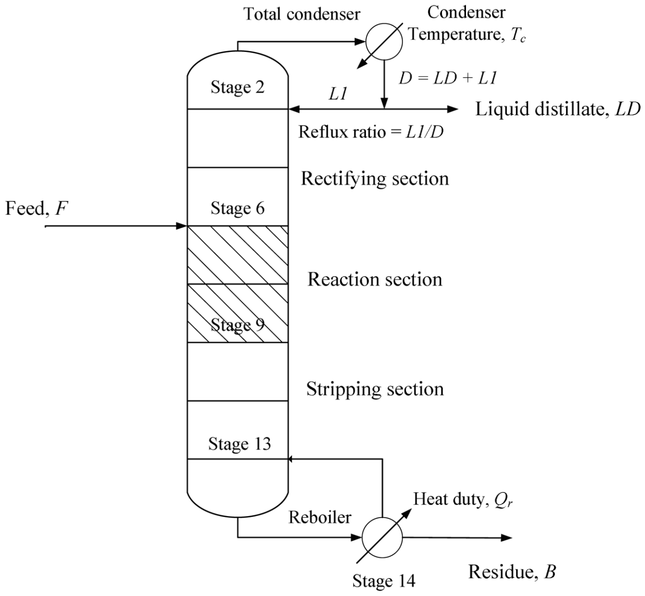

Fig. 1. The configuration of a reactive distillation column.

based on the predictive Soave-Redlich-Kwong equation of state is employed. This correlation has been widely used for the prediction of enthalpy and other thermodynamic properties. Interaction parameters for computing multi-component vapor-liquid and liquid-liquid equilibriums are predicted by using the UNIFAC activity coefficient model [Sneesby et al., 1997].

Fig. 1 shows a typical configuration of the RD column used in the simulation studies. The column contains a total of 14 stages counted down from the top. This includes a total condenser and a partial reboiler as respectively shown in stage 1 and 14. The RD column is divided into three sections: rectifying, reaction and stripping sections. The chemical reactions are assumed to occur in the liquid phase in the reaction section represented by 4 reactive stages (stage 6-9). The feed is introduced at the top of the reaction section (stage 6). To be noted is that such a column configuration is determined as a preliminary simulation study; however, it can be adjusted to meet optimal performance of the RD column. Table 1 summarizes the column parameters and feed conditions under the standard operation. The mixed TAA-EtOH feed stream enters the RD column at 25 °C. It should be remembered that two additional input parameters of the column configuration are needed to be specified for the simulation of the RADFRAC column [Quitain, et al., 1999]. These can be chosen from the following parameters: heat duty at the reboiler (Q_r), condenser temperature (T_c), ratio of total distillate flow to feed (D/F) and reflux ratio (R). Here, the parameters, Q_r and R, are selected in our study as they can be practically manipulated in real operation.

Table 1. Feed conditions and specification of reactive distillation column under the standard condition

Feed conditions		Column specification	
Temperature [K]	298	Rectification stages	4
Flow rate [mol/s]	2.71×10^{-3}	Reaction stages	4
Mole fraction [-]		Stripping stages	4
1) EtOH	0.5	Total stages	14
2) TAA	0.5	Catalyst weight per stage [kg]	0.125
Pressure [kPa]	101.3	Pressure [kPa]	101.3
		Reflux ratio (R) [-]	2
		Reboiler duty (Q_r) [W]	52

2. Kinetic Model

In this work, a non-equilibrium kinetic model is used to describe the reactions occurring in the reaction stages. TAEE is produced by the direct etherification of TAA with EtOH in the liquid phase over Amberlyst 15, a commercial acid catalyst, and is inhibited by two undesired side reactions: the dehydration of TAA to IA and the etherification of the IA produced to TAEE. Although IA can be represented by two isomers: 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B), they are lumped together with the properties of the major isomer 2M2B [Rihko and Krause, 1993]. Kinetic and thermodynamic studies have shown that the etherification of EtOH with TAA and IA and the dehydration of TAA are reversible and equilibrium-limited. The etherifications in Eqs. (1) and (3) are exothermic while the dehydration in Eq. (2) is endothermic.

The reaction scheme for the liquid phase synthesis of TAEE from TAA and EtOH taking place in the reaction section can be summarized as follows:

$$\mathrm{TAA+EtOH \leftrightarrow TAEE+H_2O} \tag{1}$$

$$\mathrm{TAA \leftrightarrow IA+H_2O} \tag{2}$$

$$\mathrm{IA+EtOH \leftrightarrow TAEE} \tag{3}$$

The kinetic models of the above reactions on Amberlyst 15 are taken from Aiouache and Goto [2003a]. In their work, the rate equations expressed in activity form are based on the power law model of which the validity was verified with the experimental data. However, the expressions for the rate equations in mole fraction form are required in Aspen Plus. For this reason, the kinetic parameters for the liquid phase synthesis of TAEE reported by Aiouache and Goto [2003a] are multiplied with the average activity coefficients of each component. The new sets of the kinetic parameters and the equilibrium constants shown in Table 2 are derived from the Arrhenius and Van't Hoff plots for various temperatures. Therefore, the rate equations of the reactions (1) to (3) can be expressed in terms of mole fractions as follows.

$$r_{EtOH} = -m_r Q\left[k_1\left(x_{EtOH}x_{TAA} - \frac{x_{TAEE}x_{H_2O}}{K_{eq1}}\right) + k_3\left(x_{IA}x_{EtOH} - \frac{x_{TAEE}}{K_{eq3}}\right)\right] \tag{4}$$

$$r_{TAA} = -m_r Q\left[k_1\left(x_{EtOH}x_{TAA} - \frac{x_{TAEE}x_{H_2O}}{K_{eq1}}\right) + k_2\left(x_{TAA} - \frac{x_{IA}x_{H_2O}}{K_{eq2}}\right)\right] \tag{5}$$

Table 2. Expressions of the parameters used in the kinetic model

Parameters	Activation energy, E_a (kJ/mol)
$k_1=\exp(15.189-6597.3/T)$	54.9
$k_2=\exp(14.490-6372.9/T)$	53.0
$k_3=\exp(22.540-9184.6/T)$	76.4
$K_{eq1}=\exp(-0.471+524/T)$	
$K_{eq2}=\exp(5.16-1824.3/T)$	
$K_{eq3}=\exp(-5.64+2349/T)$	

$$r_{IA}=r_{EtOH}-r_{TAA} \tag{6}$$

$$r_{TAEE}=-r_{EtOH} \tag{7}$$

$$r_{H_2O}=-r_{TAA} \tag{8}$$

where Q is ion-exchange capacity of Amberlyst 15 (Q=4.9 mol-H^+/kg).

3. Model Validation

In order to use the RADFRAC model from Aspen Plus for simulating a reactive distillation with confidence, the reliability of the model is tested by comparing the simulated results obtained in this study with the experimental data from Aiouache and Goto [2003b]. With the same standard experimental conditions from Table 2 in their paper, results of the simulation run in comparison to the experimental data are shown in Table 3. It can be seen that the compositions in the distillate and the residue, calculated by Aspen Plus, are in good agreement with the experimental data. The small difference may be due to the modified kinetic parameters that are based on the mole fraction rate expression.

RESULTS AND DISCUSSION

1. Standard Condition

The reactive distillation and kinetic model mentioned in the previous section are used in the simulation of the RD column. Under the standard conditions given in Table 1, the simulated results of mole fraction profiles of each component with the column stage number are shown in Fig. 2. It can be seen that 27.93 mol% of TAEE can be obtained in the liquid residue of the RD while the distillate comprises mostly IA (87.67 mol%) and a little amount of EtOH and H_2O. Fig. 2 also presents the temperature profile inside the column. The temperature at the reboiler and the condenser is 353 and 309 K, respectively. It is noticed that the temperature profile is rather smooth in the reaction section due to a mild reaction heat released.

Table 3. Comparison of simulated results and experimental data from Aiouache and Goto [2003b]

Components	Distillate (mole fraction)		Residue (mole fraction)	
	Experimental	Simulation	Experimental	Simulation
TAEE	0.047	0.04	0.185	0.167
TAA	0.046	0.042	0.227	0.231
EtOH	0.139	0.103	0.309	0.345
IA	0.727	0.812	0	0
H_2O	0.041	0.051	0.279	0.282
T (K)	313.1	313.6	351.2	355.2

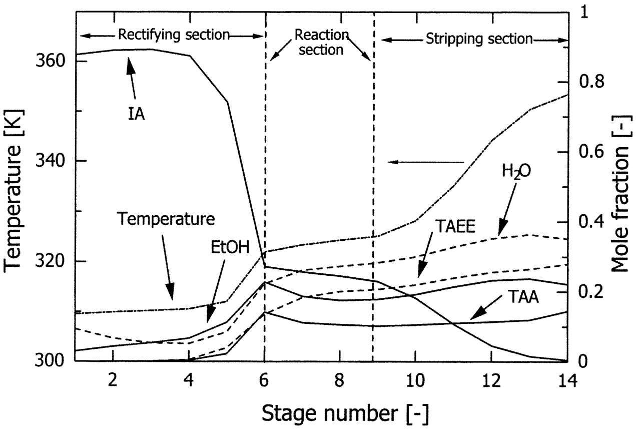

Fig. 2. Mole fraction and temperature profiles inside the column at the standard operating condition (Feed molar flowrate= 2.71×10^{-3} mol/s, Reflux ratio=2, Catalyst=0.5 kg, Feed TAA : EtOH=1 : 1).

To operate the RD column efficiently, it is important to convert TAA into the desired product (TAEE) and to obtain TAEE in the liquid residue as high as possible. Thus, the conversion of TAA and the selectivity of TAEE as defined below are considered to compare the performance of the reactive distillation.

$$\text{Conversion of TAA} = \frac{\text{difference in molar flowrate of inlet and outlet of TAA}}{\text{feed molar flowrate of TAA}} \times 100\%$$

$$\text{Selectivity of TAEE} = \frac{\text{molar flowrate of TAEE in residue}}{\text{total molar flowrate of TAEE and IA in distillate and residue}} \times 100\%$$

The conversion of TAA and the selectivity of TAEE at the standard condition are 71.29% and 77.87%, respectively. In the following sections, key design and operating variables are varied to study their effects on the conversion of TAA and the selectivity of TAEE.

2. Effects of Design Variables

As stated earlier, the specification of the reactive distillation column given in Table 1 for the synthesis of TAEE is a preliminary configuration. To find optimal design variables for the operation of the RD, simulations are carried out to study the effects of these variables on the RD performance. The important design variables considered here include the number of rectifying, reaction and stripping stages.

2-1. Number of Reaction Stages

The function of a reaction section within the RD column is to provide a location where the reactions occur. Fig. 3 shows the effect

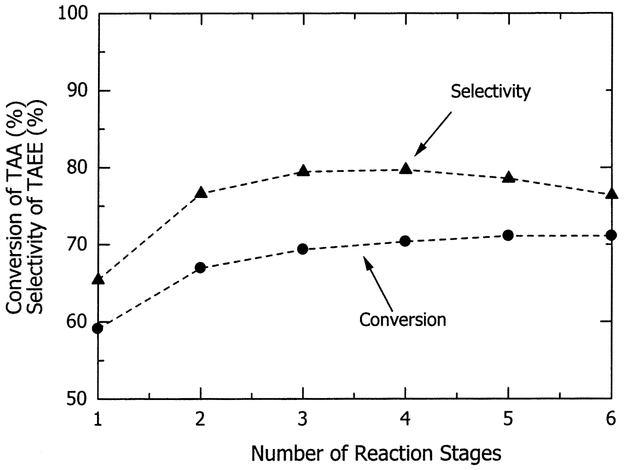

Fig. 3. Effect of the number of reaction stages on the reactive distillation performance.

of the number of reaction stages (1-6 stages) on the RD column performance. It is noted that all other design and operating variables such as the number of rectifying and stripping stages, reflux ratio, reboiler duty and feed conditions are kept at the values of the standard condition and the feed is still introduced at the top of the reaction section. The simulated results show that by using more reaction stages the conversion of TAA increases but the selectivity of TAEE decreases. According to Fig. 3, it can be seen that 4 reaction stages give a better performance in term of the selectivity. Increasing a number of reaction stages above the optimal value results in more IA production, leading to a decrease in the selectivity of TAEE. This is to be expected as an excess number of reaction stages can promote undesired dehydration of TAA to IA (Eq. (2)). Although IA can further react with EtOH to form TAEE according to Eq. (3), most of IA is in gas phase and its solubility in the liquid mixture is low under the standard operating pressure (0.1 MPa). As a consequence, a slight amount of TAEE is produced from the liquid phase etherification of IA (Eq. (3)). From this reason, the number of reaction stages of 4 is used in the column configuration for the next simulations.

2-2. Number of Rectifying Stages

The purposes of a rectification section are to remove light components from the reaction zone, to prevent loss of TAEE in the distillate and to recycle the unreacted reactants back to the reaction section in the RD column. The effect of the number of the rectifying stages on the selectivity of TAEE and the conversion of TAA is demonstrated in Fig. 4. It is found that even though the TAA conversion increases with the increase of the number of rectification stages, the selectivity of TAEE decreases. This can be explained by the fact that with the increased number of the rectifying stages, IA, the lightest component, is more removed from the reaction section, decreasing the concentration of IA in the reaction zone. This causes the equilibrium equation of Eq. (2) to shift in the forward reaction and thus, the conversion of TAA becomes higher whereas the selectivity of TAEE becomes lower. From the simulated results shown in Fig. 4, it seems that the increase of the number of rectifying stages has no significant effects on the performance of the reactive distillation. Therefore, no rectification stage is recommended for this system.

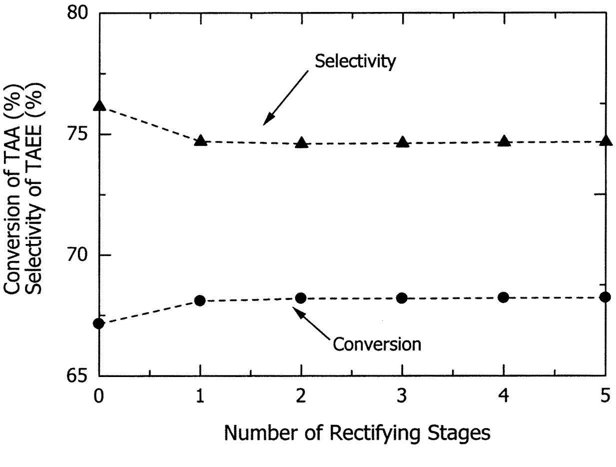

Fig. 4. Effect of the number of rectifying stages on the reactive distillation performance.

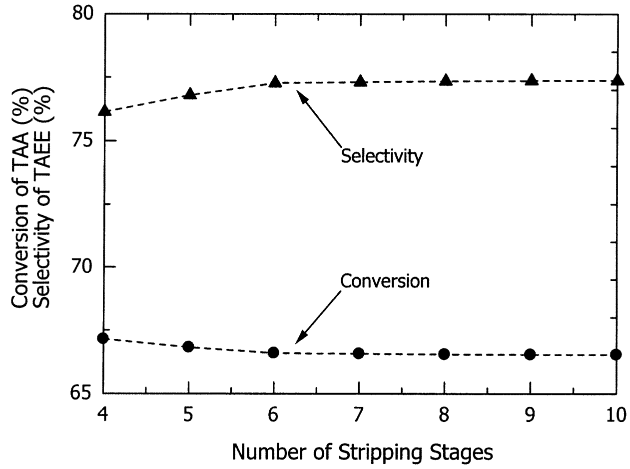

Fig. 5. Effect of the number of stripping stages on the reactive distillation performance.

2-3. Number of Stripping Stages

In a reactive distillation, the number of stripping stages is adjusted to ensure that a satisfactory separation is achieved. The main function of the stripping section is to purify the TAEE product in the residue. It can be seen from Fig. 5 that the TAA conversion slightly decreases as the number of stripping stages is increased from 4 to 10 stages; however, the selectivity of TAEE shows a contrary trend. Increasing the stripping stages causes more TAA contents removed from the reaction section to the residue and therefore, the TAA conversion is decreased. In addition, the increased stripping stages decrease the concentration of TAEE in the reaction zone, shifting the equilibrium of the etherification of TAA in the forward direction. As a result, the selectivity of TAEE becomes higher. Fig. 5 also shows the mole fraction of TAEE in the residue. The TAEE purity in the residue exhibits a similar response to the change in the selectivity; it gradually increases to 26% mole fraction of TAEE as more stages are added. The results for the studied system indicate that both the two parameters, the selectivity and purity of TAEE, earn benefits from the increase in the number of stripping stages. Therefore, the optimum configuration would be 8 stripping stages.

At this stage, the optimal design variables for the reactive distillation are no rectifying, 4 reaction and 8 stripping stages. It should be noted that the location of feed consisting of TAA and EtOH is still fixed at the top tray of the reaction section. This suitable configuration will be further used in order to examine the effects of operating variables: reflux ratio, catalyst weight, operating pressure and location of feed. This provides beneficial information for improving an operation of the reactive distillation.

3. Effects of Operating Variables

3-1. Reflux Ratio

Fig. 6 presents the effect of the reflux ratio on the performance of the reactive distillation. It can be seen from this figure that an increase in the reflux ratio from 2 to 16 causes a decrease in the conversion of TAA; however, it has a positive effect on the selectivity of the desired TAEE product in residue as the selectivity increases from 81.59% to 94.22%. This is because the increase of the reflux ratio increases the concentration of IA in the reaction section where it can react with EtOH to produce more TAEE. It is noticed that IA

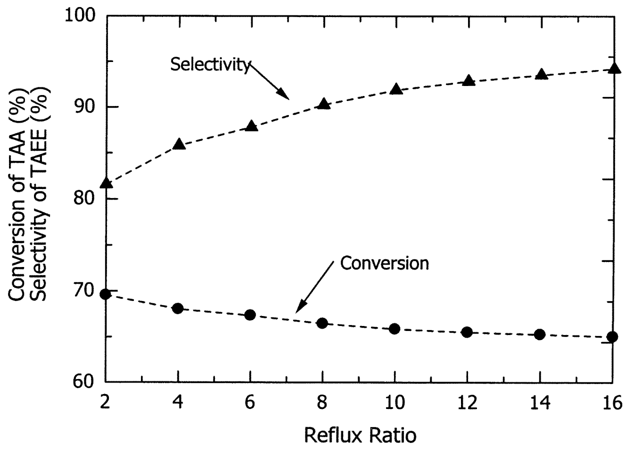

Fig. 6. Effect of the reflux ratio on the reactive distillation performance.

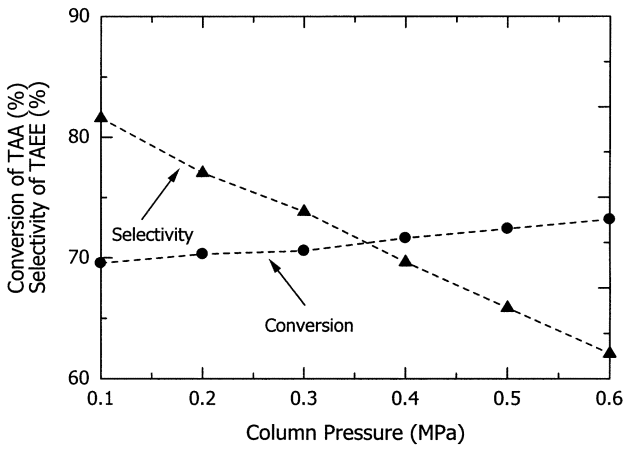

Fig. 8. Effect of the column pressure on the reactive distillation performance.

is a major component in the distillate. Moreover, some contents of unreacted reactants, EtOH and TAA, in the distillate are recycled back to the reaction section, leading to higher selectivity of TAEE. However, it should be noted that some extents of the reflux IA can react with H_2O (reverse reaction of Eq. (2)) generating more TAA. This is probably a reason for the slight decrease of the TAA conversion.

3-2. Catalyst Weight

Since a catalyst is used to accelerate the reaction rate and to influence the selectivity, the effect of the amount of total catalyst in the reaction section on the performance of RD column is studied. Fig. 7 shows that as the total amount of catalyst in the reaction section increases, the amount of TAA converted to TAEE as well as the selectivity of TAEE increase. However, it is observed that when the catalyst weight is more than 0.4 kg, the conversion of TAA and the selectivity of TAEE are slightly improved. This indicates that the reactions are approaching equilibrium-limited conditions. It should be noted that the catalyst is uniformly distributed along the reaction stages in this study, and that although the increase in the amount of catalyst has a positive effect on the performance of the reactive distillation, other factors, e.g., cost of catalyst and capacity of column should also be considered in selecting the appropriate amounts of catalyst in the reaction section.

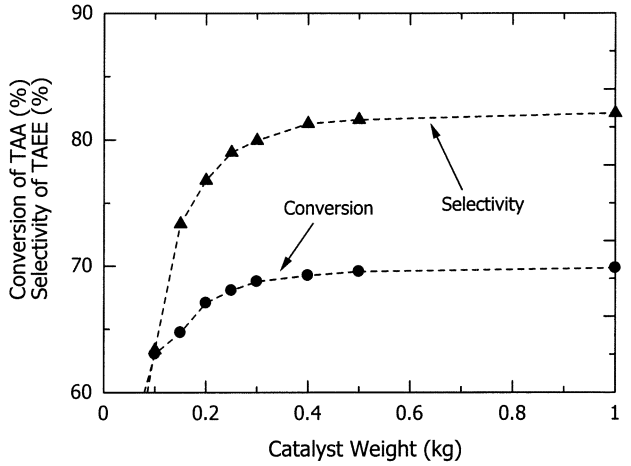

Fig. 7. Effect of the catalyst weight on the reactive distillation performance.

3-3. Operating Pressure

The operating pressure is one of the key operating parameters of a distillation column. The choice of operating pressure for the reactive distillation column depends on many considerations such as overhead temperature, bottom temperature and reaction temperature in the system. Since chemical reactions take place in the liquid phase, the reaction temperature is close to the boiling point of the liquid phase flowing around the catalyst. Fig. 8 shows the influence of the column pressure on the TAA conversion and TAEE selectivity. It is found that as the pressure increases from 0.1 to 0.6 MPa, the reaction stage temperature increases linearly from 48 to 100 °C (data not shown). From the kinetic parameters given in Table 2, one would expect that rate of the dehydration of TAA to IA, Eq. (2), is more pronounced when the reaction temperature increases, resulting in the lower selectivity of TAEE as can be seen from Fig. 8. However, the conversion of TAA is quite insensitive to the operating pressure. This suggests that the operating pressure of 0.1 MPa is suitable for the reactive distillation to synthesis TAEE. It should be noted that operation of the reactive distillation column at lower than the atmospheric pressure (0.1 MPa) is not attractive due to high operating cost. In addition, it was found from our preliminary results that a lower pressure is not beneficial to the performance of this system.

3-4. Feed Stage Location

Since the location of the feed can be adjusted to make the best separation and the most favorable reaction conditions, simulations are performed to investigate the effects of the feed location of TAA and EtOH on the RD performance. The cases where the feed reactants (TAA and EtOH) are separated in two streams on the reaction section are compared with the one that both TAA and EtOH are mixed in one feed stream as in the standard conditions. The results are summarized in Table 4. It has been known that when the feed components are separated in two different locations, the reactant with lower boiling point is normally introduced at the lower stage of the reaction section, compared to the higher boiling point. However, it is found here that feeding TAA and ethanol together at the top of the reaction section offers the highest conversion of TAA

Table 4. Effect of feed separation on the TAA conversion and the TAEE selectivity

Feed location		Reaction stage	TAA conversion	TAEE selectivity	Residue composition (%mole fraction)				
TAA	EtOH				TAEE	TAA	EtOH	IA	H_2O
2	2	2-5	69.64	81.71	28.68	15.38	21.3	0	34.63
2	3	2-5	69.52	79.16	27.82	15.17	22.61	0	34.38
2	4	2-5	67.88	74.50	25.57	16.04	24.98	0	33.4
2	5	2-5	61.06	60.53	18.74	19.48	31.96	0	29.71

(69.64%) and selectivity of TAEE (81.71%). It is noticed that separating the feed components decreases both the TAA conversion and TAEE selectivity. This is probably due to the fact that the residence time of the reactants is decreased when the location of the EtOH feed in the reaction section is below, compared to that of the TAA feed; EtOH will travel down to the bottom part of the column without being reacted as shown in Table 4.

CONCLUSION

The liquid phase synthesis of *tert*-amyl ethyl ether (TAEE) from *tert*-amyl alcohol (TAA) and ethanol in a reactive distillation column has been studied. The simulation of this process using a rate-based kinetic expression and an equilibrium stage model is performed using Aspen Plus. The influences of key design variables on the performance of the reactive distillation are investigated. The results indicate that the optimal design of the column consists of no rectifying, 4 reaction, and 8 stripping stages. In order to operate the reactive distillation column efficiently, the effects of various operating parameters on the reactive distillation performance are analyzed. It has been found that the reflux ratio and operating pressure are the most important factors affecting the conversion of TAA and the selectivity of TAEE.

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NOMENCLATURE

D : total distillate flowrate (=LD+L1) [mol/s]
D/F : distillate to feed ratio [-]
F : feed flowrate [mol/s]
k_i : kinetic constant base on mol fraction [mol/(s mol-H^+)]
K_i : equilibrium constant [-]
LD : liquid distillate flowrate [mol/s]
L1 : liquid flowrate to return from stage 1 to stage 2 [mol/s]
m_r : mass of dry ion-exchange resin [kg]
Q : ion-exchange capacity (=4.9) [mol-H^+/kg-dry resin]
Q_r : reboiler duty [W]
R : reflux ratio [-]
r_i : reaction rate [mol/(s kg-dry resin)]
T_c : condenser temperature [K]
VD : vapor distillate flowrate [mol/s]
x_i : mole fraction of component i [-]

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