Effect of Number of Fractionating Trays on Reactive Distillation Performance

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Sneesby et al. recently suggested that adding trays in the stripping and rectifying sections of a reactive distillation column can degrade performance. This effect, if true, is not only counterintuitive, but very disturbing because it suggests that the design of reactive distillation columns cannot use conservative estimates of tray numbers, that is, we cannot simply add excess trays, as in conventional distillation. The problem is compounded by the uncertainty in vapor–liquid equilibrium data and tray efficiencies. This implies that developing reactive distillation columns would require extensive experimental work at the pilot-plant and plant stages to find the numbers of stages offering the best performance. Such a scenario would mean long and expensive development programs. This article explores the effect of the number of trays in the rectifying and/or stripping sections of reactive (catalytic) distillation columns. Three reactive distillation systems are used: an ideal hypothetical system, the ETBE system, and the methyl acetate system. Contrary to the published results, it is demonstrated that additional trays do not degrade performance. Two degrees of freedom available in all cases must be carefully chosen for fair comparisons.

Introduction

Reactive distillation has been employed in industry for many decades, but its area of application has grown significantly in the last decade. Reactive distillation can reduce capital and energy costs in some systems, particularly when reactions are reversible or when the presence of azeotropes makes conventional separation sections complex and expensive. Of course, the reaction temperatures must be suitable for vapor and liquid phases to exist and the volatilities of the reactants and products must be such that the products can be removed while containing the reactants in the column.

Much of the pioneering theoretical developments have come from Doherty and coworkers (Barbosa and Doherty, 1988a,b,c; Doherty and Buzad, 1992; Buzad and Doherty, 1995; Okasinski and Doherty, 1998). Other workers in the field include Ciric and Gu (1994) and Subwalla and Fair (1999). The best-known industrial application, the production of methyl acetate, is reported by Agreda et al. (1990) from Eastman Chemical Co. The literature up to 1992 was reviewed by Doherty and Buzad (1992). Almost all of the work has considered only steady-state design. Only a handful of articles have studied dynamics and control (Bock et al., 1997; Bartlett and Wahnschafft, 1999; Kumar and Daoutidis, 1999; Sneesby et al., 1999).

A most interesting and intriguing article by Sneesby et al. (1998) appeared recently. This article claimed that increasing fractionation was detrimental to the performance of an ethyl tert-butyl ether (ETBE) reactive distillation column. The authors presented several cases in which reducing the number of trays in the stripping and rectifying sections resulted in an increase in conversion.

These findings have potentially very important implications for reactive distillation systems. In conventional distillation we normally use a design heuristic to determine the number of theoretical trays, for example, twice the minimum number. Then an estimate of tray efficiency is made to determine the actual trays. Finally, conservative designers add a few additional trays to provide for the everpresent uncertainties in vapor–liquid equilibrium data, in tray efficiency estimations, in product quality requirements, and in sales forecasts. This conservative approach could not be taken in reactive distillation if adding additional trays resulted in degradation of performance.

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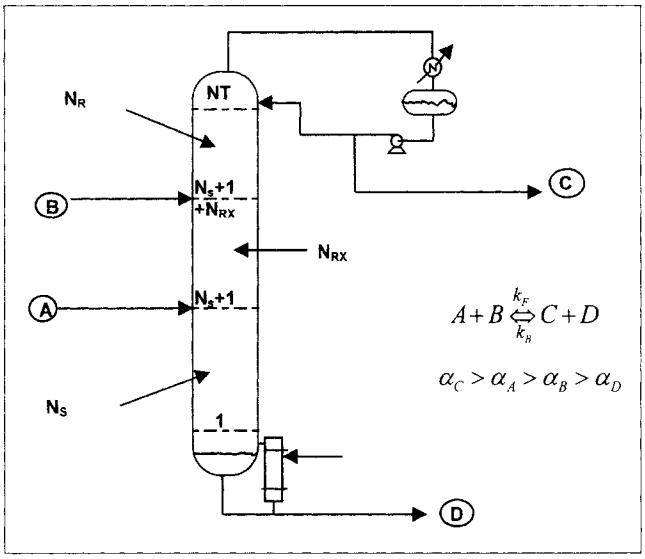

Figure 1. Ideal reactive distillation column.

Intuition would lead one to think that adding additional trays should improve performance, at least the fractionation performance of the column. Let us consider the classic reactive distillation column shown in Figure 1. The column has N_s trays in the stripping section, N_{RX} trays in the reactive section (containing the catalyst), and N_R trays in the rectifying section. The reversible reaction occurring on the reactive trays is

$$A + B \Leftrightarrow C + D. \tag{1}$$

The volatilities are such that the products C and D are the lightest and heaviest, respectively, in the system.

$$\alpha_C > \alpha_A > \alpha_B > \alpha_D. \tag{2}$$

The reactants A and B are intermediate boiling between the products. Therefore the fresh feed stream F_{0A} containing reactant A is fed at the bottom of the reactive zone, and the fresh feed stream F_{0B} containing reactant B is fed at the top of the reactive zone.

The purpose of the stripping and rectifying sections is to keep the reactants from leaving the column. One would expect this job would be made easier by having more trays in these sections. So the detrimental effect reported in the literature is certainly counterintuitive.

ETBE Literature Study

The system studied by Sneesby et al. (1998) is the production of ETBE. The basic reaction involves ethanol reacting with isobutylene. This system has several aspects that make it complex.

1. The vapor–liquid equilibrium behavior is nonideal.
2. The feed comes from a prereactor, so it is a mixture of product and reactants.
3. The feed also contains an inert component *n*-butylene, which is taken overhead in the column.
4. An excess of ethanol is typically used to drive the reaction.
5. The total feed stream is introduced on one tray, unlike the classic case where the two reactants are fed at different locations.

The article in the literature presents a series of cases in which several parameters were varied. Table 1 summarizes the various cases. Note the higher conversions obtained in Cases 4 and 5 when fewer trays are used.

However, the authors chose the variables that are fixed in the various cases in a somewhat arbitrary manner, and we claim this is the source of the flaw in the reported conclusions.

Degrees of Freedom

Any simple two-product distillation column has two degrees of freedom, that is, two variables can be specified. This applies to a fixed column (total trays and feed trays fixed) operating at a given pressure with given feeds (flow rates, compositions, and thermal conditions). In the design of a conventional distillation column, we typically fix these two degrees of freedom by specifying the impurities of the key components in the distillate and bottoms products ($x_{D,HK}$ and $x_{B,LK}$). Of course there must be more trays in the various sections of the column than the minimum for there to be a feasible solution.

Table 1. ETBE Results in the Literature

	Isobutylene-Rich Feed			Isobutylene-Lean Feed		
	Design 1	Design 4	Design 5	Design 1	Design 4	Design 5
$N_s/N_{RX}/N_R$	**14/7/7**	**8/4/4**	**8/4/4**	**14/7/7**	**8/4/4**	**8/4/4**
Conversion	89.7	91.1	94.7	94.4	97.1	97.6
Specifications:						
Reflux ratio	1.2	1.2	1.8	0.8	0.8	1.2
Total butylene in bottoms (wt. %)	0.1	0.1	0.1	0.1	0.1	0.1
Compositions: (wt. %)						
Distillate isobutylene	5.90	5.60	5.70	0.85	0.31	0.10

Basis: Pressure = 7 bar; production rate = 5,000 kg/h ETBE; 5% stoichiometric excess of ethanol; single feed to top of stripping section.

The paper in the literature results presented in Table 1 apply when the degrees of freedom have been fixed by specifying the impurity of total butylenes in the bottoms ($x_{B,iC4=} + x_{B,nC4=}$) and the reflux ratio (RR). This choice of specifications does not limit the losses of reactants out of the top or bottom of the column. Thus, conversion is not held constant when the degrees of freedom are chosen in this manner. Table 1 shows that the isobutylene concentration in the distillate decreases in Cases 4 and 5. *Reducing the loss of this limiting reactant is what is causing the increase in conversion, not the reduction in the number of trays.*

More realistic comparisons can be achieved by selecting the degrees of freedom in such a way that reactant losses are limited. The most straightforward way is to specify the conversion and the purity of one of the product streams for a given feed flow rate and composition. In the ETBE case, we suggest specifying the conversion and the mol fraction of ETBE in the bottoms ($x_{B,ETBE}$). These two specifications set the bottoms product flow rate, since all of the ETBE goes out the bottom. The remaining material in the bottoms is mostly unreacted ethanol, since it is heavier than the butylenes. We have guaranteed that the desired amount of ETBE will be produced, which means that the comsumption of both reactants is fixed.

It is important to note that there is no guarantee that the desired conversion can be achieved in the column as specified unless there are sufficient number of reactive stages with sufficient holdup (or amount of catalyst), and there are more than the minimum number of stripping and rectifying stages. So we could start with a conservative design (many trays in all three sections) and know that the desired conversion can be achieved.

The effectiveness of using the specifications just discussed is demonstrated in the following sections.

Ideal Reactive Distillation System

The first system studied is one in which we strip away all the complexities of nonideal behavior and consider a system with constant relative volatilities, equimolal overflow, fixed heat of reaction and heat of vaporization, saturated liquid feed and reflux, and constant pressure. The classic case is considered with two pure reactant feed streams of components A and B fed to trays at the top and bottom of the reactive zone in the column. The reversible reaction $A + B \Leftrightarrow C + D$ occurs in this section, which contains N_{RX} trays. The rectifying section above the reactive section contains N_R trays, and the stripping section below the reactive zone contains N_S trays. The relative volatilities are $\alpha_C > \alpha_A > \alpha_B > \alpha_D$, so product C is removed in the distillate stream and product D is removed in the bottoms.

Table 2. Physical Properties for Ideal Systems

Activation energy (cal/mol)	Forward	30,000				
	Backward	40,000				
Specific reaction rate at 366 K (kmol·s^{-1}·kmol^{-1} ·(mol·frac.)$^{-2}$)	Forward	0.008				
	Backward	0.004				
Heat of reaction (cal/mol)		−10,000				
Heat of vaporization (cal/mol)		6,944				
Relative volatilities	α_C		8			
	α_A		4			
	α_B		2			
	α_D		1			
Vapor pressure constants			C	A	B	D
	A_{VP}		13.04	12.34	11.45	10.96
	B_{VP}		3,862	3,862	3,862	3,862

$\ln(P_j^s) = A_{VP,j} - B_{VP,j}/T$, where T is degrees K and P_j^s is the vapor pressure of pure component j in bar.

System parameters and model

The forward and backward specific reaction rates (kmol · sec^{-1} kmol^{-1}) on tray n are given by

$$k_{Fn} = a_F \exp\left(\frac{-E_F}{RT_n}\right) \tag{3}$$

$$k_{Bn} = a_B \exp\left(\frac{-E_B}{RT_n}\right), \tag{4}$$

where a_F and a_B are the preexponential factors, E_F and E_B are the activation energies, and T_n is absolute temperature on tray n. Table 2 gives kinetic and physical property data for the system.

The net reaction rate for the production of C (kmol/s) on tray n in the reactive zone is given by

$$R_{Cn} = M_n(k_{Fn}x_{nA}x_{nB} - k_{Bn}x_{nC}x_{nD}), \tag{5}$$

where M_n is the liquid molar holdup on the tray. If catalytic distillation is considered, the weight of catalyst on the tray would be used. It should be noted that tray holdup is assumed to be constant, so there is no effect of liquid flow rate on the M_n term in the reaction-rate expression, even though the reaction considered in this ideal case is kinetically limited. In the ETBE and methyl acetate cases considered in the next section, solid catalyst is used and thermodynamic reaction equilibrium is assumed. Therefore, the effect of liquid holdup on the reaction rate does not exist.

The component balance on tray n for product C is (numbering trays from the bottom):

$$L_{n+1}x_{n+1,C} + V_{n-1}y_{n-1,C} + R_{Cn} = L_n x_{n,C} + V_n y_{n,C} \tag{6}$$

Similar balances apply for the other three components with the appropriate sign for the reaction-rate term.

The vapor−liquid equilibrium is assumed to be ideal. See Table 2 for vapor-pressure data:

$$P = x_{nA}P_A^s(T_n) + x_{nB}P_B^s(T_n) + x_{nC}P_C^s(T_n) + x_{nD}P_D^s(T_n), \tag{7}$$

where total pressure P and vapor pressures P^s are in bar. The column pressure is fixed at 9 bar.

Since equimolal overflow is assumed, the vapor and liquid rates are constant through the stripping and rectifying sections. However, these rates change from tray to tray in the reactive zone because the heat of reaction vaporizes some

Table 3. Base Case Conditions: Ideal System

Flow rate (kmol/s)				
Fresh feed F_{0A}	0.0126			
Fresh feed F_{0B}	0.0126			
Reflux	0.0341			
Vapor boilup	0.0295			
Top tray vapor	0.0467			
Distillate	0.0126			
Bottoms	0.0126			
Pressure (bar)	9.0			
Tray holdup (kmol)	1.0			
Tray number				
Stripping	10			
Reactive	10			
Rectifying	10			
Temperature (K)				
Base	438			
Top stripping	394			
Top reactive	396			
Top rectifying	358			
Composition (mol fraction)	*A*	*B*	*C*	*D*
Distillate	0.0410	0.0090	0.9500	0.0000
Bottoms	0.0084	0.0416	0.0000	0.9500

liquid on each tray:

$$V_n = V_{n-1} - R_{Cn}\frac{\lambda}{\Delta H_v} \tag{8}$$

$$L_n = L_{n+1} + R_{Cn}\frac{\lambda}{\Delta H_v}, \tag{9}$$

where λ is the heat of reaction ($-10{,}000$ cal/mol) and ΔH_v is the latent heat of vaporization (6,944 cal/mol).

The base-case conditions are given in Table 3. The two fresh feed flow rates are each 0.0126 kmol/s of pure reactants. Conversion is specified to be 95%, so the amounts of C and D produced are (0.95)(0.0126). The amounts of A and B unreacted are (0.05)(0.0126). Remember that essentially all the C leaves in the distillate and all the D leaves in the bottoms because of the relative volatilities. Composition profiles are given in Figure 2.

The first degree of freedom chosen is the 95% conversion. This means that the molar flow rate of product C out of the top of the column must be (0.95)(0.0126). The second degree of freedom is selected to be the purity of C in the distillate. If this is selected, the system is completely specified.

It is important to realize that this purity specification has a limited practical range. With the conversion set, there is only a given amount of unreacted reactants. These must leave in either the distillate or the bottoms. So as the purity of the distillate is increased, more of the reactants must leave in the bottoms. For example, suppose we set the desired purity at $x_{D,C} = 0.95$. The distillate will contain (0.95)(0.0126) kmol/s of component C and (0.05)(0.0126) kmol/s of components A and B (mostly A, since it is lighter). Therefore, the distillate flow rate is 0.0126 kmol/s.

Other purity specifications would change distillate (and bottoms) flow rates. For example, suppose conversion is again set at 95%, but the distillate purity is specified to be 98%

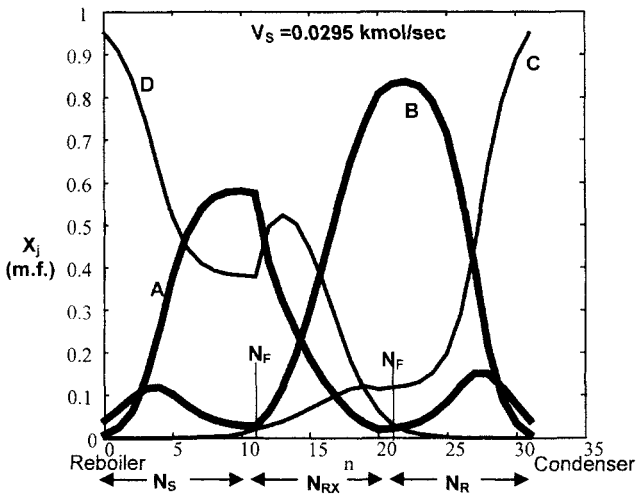

Figure 2. Base case composition profiles (ideal system).

component C. Now the distillate flow rate is (0.95)(0.0126)/0.98 = 0.012214 kmol/s and the bottoms flow rate is 0.0252 − 0.012214 = 0.012986 kmol/s. The impurity in the distillate is (0.02)(0.012214) = 0.000244 kmol/s, leaving (0.05)(0.0252) − 0.000244 = 0.00102 kmol/s of impurities in the bottoms. So the bottoms composition is (0.95)(0.0126)/0.012986 = 0.9218 mol fraction D.

Results

A steady-state solution of the nonlinear algebraic equations describing the reactive distillation column was obtained by using a relaxation method. The ordinary differential equation describing the dynamics of the system were integrated out in time until all variables stopped changing. The distillate and bottoms flow rates were calculated from the specified conversion and purity:

$$D = \frac{F_{0A}\chi}{x_{D,C}} \tag{10}$$

$$B = F_{0A} + F_{0B} - D, \tag{11}$$

where χ = conversion. The reflux flow rate is manipulated by a PI feedback controller to drive the mol fraction of C in the distillate to the desired purity. The vapor boilup is manipulated to control the base level. The reflux drum level is not controlled, but lines out at some steady-state value since the product flow rates exactly equal the feed flow rates.

Table 4 shows the effects of increasing and decreasing the stripping and rectifying trays. These results clearly show no detrimental effect of adding trays. The only change is the separation between reactants A and B. As more trays are added, the concentration of A in the bottoms decreases and the concentration of B in the distillate decreases. Thus more light material rises and more heavy material goes out the bottom. But conversion and product purities are exactly the same as trays are added. Table 5 also gives results when the desired conversion is increased to 98% and the product purity

Table 4. Effect of Changing Fractionating Trays: Ideal System; 95% & 98% Conversion

$N_S/N_{RX}/N_R$	5/10/5	10/10/10	15/10/15	5/10/5	10/10/10	15/10/15
Vapor boilup (kmol/s)	0.0294	0.0295	0.0295	0.0309	0.0297	0.0291
Reflux (kmol/s)	0.0340	0.0341	0.0341	0.0361	0.0349	0.0343
Composition (mol fraction)						
Distillate						
A	0.0279	0.0410	0.0455	0.0154	0.0194	0.0199
B	0.0221	0.0090	0.0045	0.0046	0.0006	0.0001
C	0.9500	0.9500	0.9500	0.9800	0.9800	0.9800
D	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Bottoms						
A	0.0220	0.0084	0.0050	0.0045	0.0003	0.0001
B	0.0280	0.0416	0.0450	0.0155	0.0197	0.0199
C	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
D	0.9500	0.9500	0.9500	0.9800	0.9800	0.9800

is 98%. Adding stripping and rectifying trays shows no detrimental effect.

In this section we have explored the impact of changing various parameters in the ideal system. Most importantly, we have demonstrated that adding additional rectifying and stripping trays *does not* lead to a degradation in either conversion or separation. This indicates that a conservative design (using an excess of trays) should be viable. In the next two sections, we will see if this result is also true for two systems with real chemical components: the ETBE process and the methyl acetate process.

ETBE System

The basic reaction combines ethanol and isobutylene to form ETBE:

$$iC_4^= + \text{ethanol} \Leftrightarrow \text{ETBE}. \qquad (12)$$

The $C_4^=$ feed stream contains both iso- and normal butylene, and the latter is inert. The light normal butylene inert goes overhead and the heavy ETBE goes out the bottom. Unreacted isobutylene leaves mostly in the distillate. Unreacted ethanol leaves mostly in the bottoms.

Table 5. Effect of Changing Fractionating Trays: ETBE Double Feed; 95% Conversion

$N_S/N_{RX}/N_R$	5/10/5	10/10/10	15/10/15
Vapor boilup (kmol/h)	81.10	86.15	86.54
Reflux (kmol/h)	119.70	124.44	124.41
Distillate flow rate (kmol/h)	62.00	62.00	62.00
Composition (mol fraction)			
Distillate			
$iC_4^=$	0.0314	0.0321	0.0322
$nC_4^=$	0.9644	0.9670	0.9675
EtOH	0.0042	0.0009	0.0003
ETBE	0.0000	0.0000	0.0000
Bottoms			
$iC_4^=$	0.0014	0.0003	0.0001
$nC_4^=$	0.0052	0.0011	0.0003
EtOH	0.0434	0.0486	0.0496
ETBE	0.9500	0.9500	0.9500

We consider two cases. The first has a structure that is similar to the ideal system (double feed and a stoichiometric amount of ethanol). The second case, which is similar to that reported by Sneesby et al. (1998), has a single mixed feed with an excess of ethanol. This second case would apply when a prereactor is used.

Details of the physical property data, vapor–liquid equilibrium, and reaction kinetics are given in Al-Arfaj (1999). Our basic model does not assume chemical equilibrium, because we want to be able to deal with a variety or reaction systems. Sneesby et al. (1998) assumed chemical equilibrium in their work. Therefore, we used a large excess of catalyst on the reactive trays to drive the reaction close to equilibrium. Thus, just as in the ideal case, there is no effect of liquid flow rate on the reaction rate, except through composition changes.

The system was solved rigorously using a distillation homotopy continuation method where the set of steady-state equations were solved for an easy starting problem, and then reached the actual problem by moving through a continuation parameter. The details of this method, as well as the mathematical modeling of the system, are found in Al-Arfaj (1999).

Double Feed

Figure 3 gives the flow sheet and parameter values for this system. The $C_4^=$ feed contains 40 kmol/h of isobutylene and 60 kmol/h of normal butylene. It is fed at the bottom of the reactive zone, which contains 10 trays. There are 10 stripping and 10 rectifying trays. The stoichiometric amount of ethanol (40 kmol/h) is fed to the top of the reactive zone. The conversion is specified to be 95%, so (0.95)(40) = 38 kmol/h of ETBE is produced. All of this ETBE leaves in the bottom

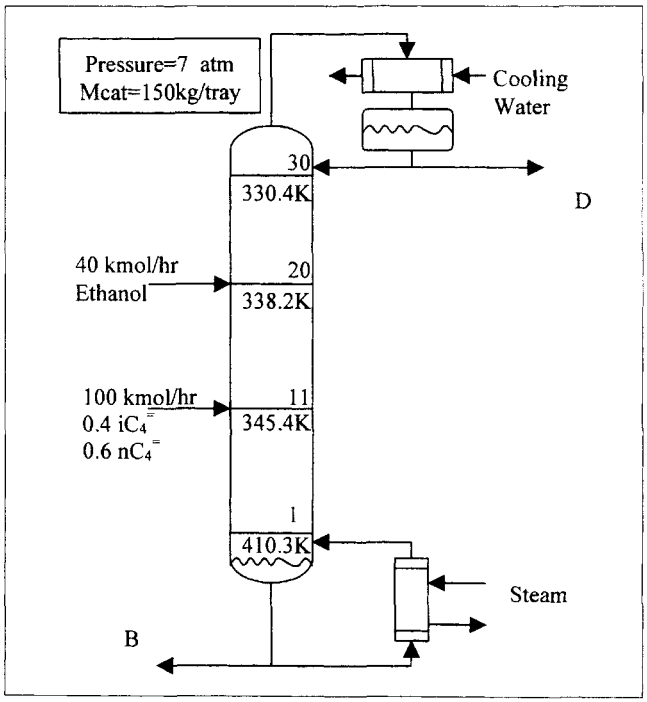

Figure 3. Double-feed ETBE reactive distillation column.

stream because of its low relative volatility. There are 2 kmol/h of ethanol unreacted and 2 kmol/h of isobutylene unreacted. There are also 60 kmol/h of inert normal butylene that must leave the system.

If a bottoms purity of 95% ETBE is specified, the bottoms flow rate is 38/0.95 = 40 kmol/h, and this stream contains 2 kmol/h of impurities (mostly ethanol, since it is heavier than the butylenes). The operating pressure is 7 atm.

The base case has 10 trays in each of the three sections. Table 5 compares results for the base case with those obtained when trays are added or removed from the stripping and rectifying sections of the column. No degradation of performance results from adding more fractionation trays.

Single feed with ethanol excess

The flow sheet of this case is shown in Figure 4. This case is essentially the same as the isobutylene-rich feed studied by Sneesby et al. (1998), with some slight differences. We neglected the butadiene component in the feed and assumed that the feed is 40% isobutylene and 60% normal butylene. The dimerization reaction of isobutylene to diisobutylene was also ignored, because only a small amount is formed.

Since we used a kinetic model for the ETBE reaction, we increased the amount of catalyst at a fixed conversion until no changes were observed in any of the variables. Figure 5 illustrates the procedure. The reflux ratio decreases as the catalyst increases, but reaches an asymptotic value of about 4.5.

In order to match Sneesby et al., we fixed the ETBE production rate and purity in the bottom to be the same as theirs (5,000 kg/h and 91.3 wt. % ETBE). To achieve these specifications, we found that a reflux ratio of 4.74 is required. Since this reflux ratio is much larger than reported by Sneesby et

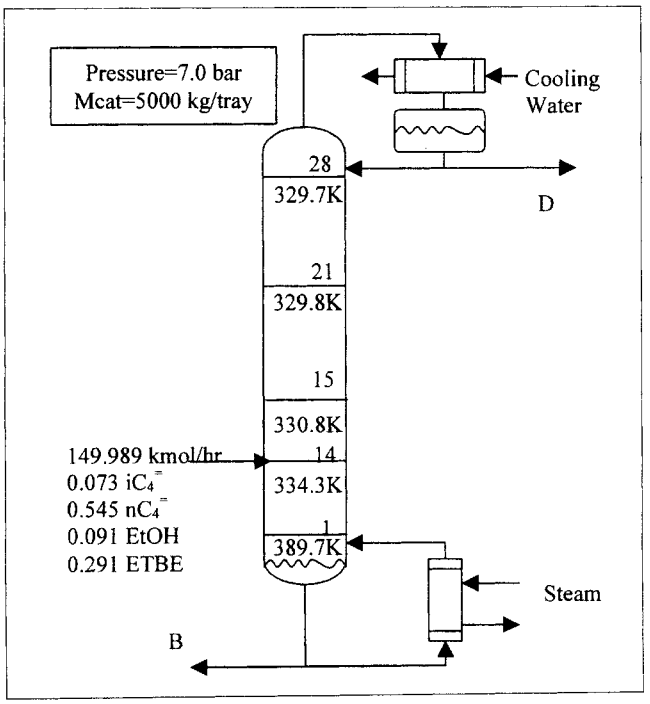

Figure 4. Single-feed ETBE reactive distillation column.

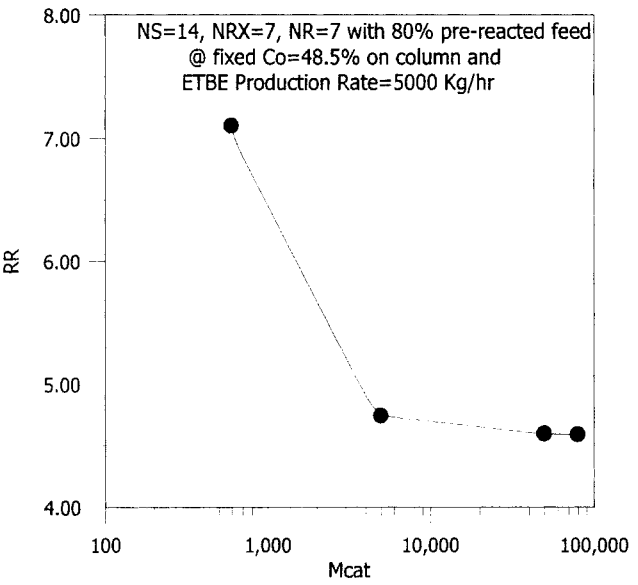

Figure 5. Effect of catalyst load on the reflux ratio at fixed conversion.

al., we used two commercial simulators to verify our results. Aspen Plus 10.1 predicted a reflux ratio of 4.75 using UNIFAC for the liquid activity coefficients and ideal vapor. HYSYS Plant 2.1 predicted a reflux ratio of 4.44 with UNIQUAC and ideal vapor.

Table 6 compares our results with those of Sneesby et al. (1998). The first case in this table gives the base design of Sneesby et al., where the isobutylene conversion in the column is 48.5% and the column has 14 stripping trays, 7 reactive trays, and 7 rectifying trays. The second case gives our results with the same column, the distillate flow rate, and the same reflux ratio. Note that the conversion is only 37.77% compared to 48.5% in the previous case.

The third case gives our results for the same column, the same ETBE purity in the bottoms, and the same conversion as those in Case 1. The required reflux ratio is much higher. Case 4 shows the effect of increasing the number of stripping and rectifying trays on Case 3. Conversion and ETBE purity are held constant as trays are added. Adding trays does not degrade performance.

The last four cases in Table 6 are identical to Cases 3 and 4, but using Aspen Plus 10.1 and HYSYS Plant 2.1. All three simulators predict that adding trays does not hurt the performance of the column, that is, the conversion and the product purity.

Table 7 shows how sensitive the problem is to the VLE package. Aspen Plus 10.1 was used with the same conversion and product purity for the base case ($N_S/N_{RX}/N_R = 14/7/7$), but with different VLE packages. The first case used modified Dortmund UNIFAC with the Redlich-Kwong-Soave equation of state. Aspen Plus 10.1 predicted a reflux ratio of 0.92. When using the original UNIFAC with the Redlich-Kwong equation of state in the second case, Aspen Plus 10.1 predicted a reflux ratio of 1.89. Finally, using the original UNIFAC with ideal vapor in the third case, Aspen Plus 10.1 predicted a reflux ratio of 4.75. These results show that the system is very sensitive to the VLE model. A designer would

Table 6. Effect of Changing Fractionating Trays: ETBE Single Feed; Equilibrium-Limited Reaction

	Sneesby		Our Result Base	Our Result High	Aspen Base	Aspen High	HYSYS Base	HYSYS High
	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 5	Case 6
$N_S/N_{RX}/N_R$	**14/7/7**	**14/7/7**	**14/7/7**	**17/7/10**	**14/7/7**	**17/7/10**	**14/7/7**	**17/7/10**
$iC_4^=$ Conversion	48.5	37.77	48.5	48.5	48.5	48.5	48.5	48.5
Reflux ratio	1.20	1.20	4.74	4.75	4.75	4.76	4.44	4.45
Composition (mol fraction)								
Distillate								
$iC_4^=$	0.0590	0.0771	0.0647	0.0647	0.0645	0.0645	0.0645	0.0645
$nC_4^=$	0.9410	0.9229	0.9353	0.9353	0.9355	0.9355	0.9355	0.9355
EtOH	< 10 ppm	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETBE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Bottoms								
$iC_4^=$	c4 = 0.002	0.0024	0.0008	0.0007	0.0001	0.0000	0.0010	0.0010
$nC_4^=$	dib = 0.008	0.0382	0.0206	0.0207	0.0204	0.0205	0.0204	0.0204
EtOH	0.1540	0.1594	0.1426	0.1426	0.1425	0.1425	0.1426	0.1426
ETBE	0.8360	0.8000	0.8360	0.8360	0.8360	0.8360	0.8360	0.8360
Distillate flow rate (kmol/h)	86.178	86.178	86.178	86.178	86.178	86.178	86.178	86.178
Reboiler duty (MW)	1.140	1.083	2.636	2.640	2.621	2.626	2.724	2.727

like to add more trays in order to take care of uncertainties in this system. This article demonstrates that additional trays can be added without degrading the performance.

The preceding results used a large amount of catalyst to achieve chemical equilibrium (5000 kg/tray). If a more realistic amount of catalyst is used (600 kg), the reaction becomes kinetically limited. Table 8 shows the kinetically limited case. The conversion, ETBE production rate, and ETBE purity in the bottoms are the same as Case 3 in Table 6. Higher reflux ratios are needed in the kinetically limited cases because higher concentrations of reactants are required on the reactive trays due to the smaller amount of catalyst. This necessitates more separation capacity (that is, higher reflux ratios) in the column. Table 8 also shows the effect of changing the number of trays. We again see no degradation of performance when additional trays are used.

Methyl Acetate System

The final system studied is the production of methyl acetate by reactive distillation. Methyl acetate (MeOAc) can be produced by the liquid-phase reaction of acetic acid (HOAc) and methanol (MeOH) over an acid catalyst. The reaction is

$$\mathrm{HOAc} + \mathrm{MeOH} \Leftrightarrow \mathrm{MeOAc} + \mathrm{H_2O}. \qquad (13)$$

The Wilson correlation and Mark's method were used to correlate the VLE, since the vapor phase contains an associating substance (acetic acid). The details of the physical properties and kinetic parameters are found in Al-Arfaj (1999). The methyl acetate system is quite similar to the ideal system, except that one of the reactants (acetic acid) is slightly heavier than one of the products (water). This means that the stripping section cannot keep the acetic acid from leaving in the bottoms if any of it leaves the base of the reactive zone. Of course, the vapor–liquid equilibrium is nonideal, with azeotropes between methanol and methyl acetate.

Methanol is fed at the bottom of the reactive zone and acetic acid at the top. Agreda et al. (1990) explained the Eastman Chemical Co. design of the methyl acetate reactive distillation column. The details of that design are found in Agreda and Partin (1984). We modified their design in two ways. Since it is easier to deal with theoretical trays, we assumed that the tray efficiency of the Eastman column was 50% and reduced the number of trays by a factor of 2. The

Table 7. Effect of VLE on Single-Feed ETBE Reactive Distillation Column Base Design ($N_S/N_{RX}/N_R$ = 14/7/7)

	$iC_4^=$ Conversion (%)	ETBE Bottoms Purity (mol %)	Reflux Ratio
MD UNIFAC + RKS	48.5	83.6	0.92
UNIFAC + RK	48.5	83.6	1.89
UNIFAC + IG	48.5	83.6	4.75

Table 8. Effect of Changing Fractionating Trays: ETBE Single Feed; Kinetically Limited Reaction

$N_S/N_{RX}/N_R$	**11/7/4**	**14/7/7**	**17/7/10**
$iC_4^=$ Conversion	48.5	48.5	48.5
Reflux ratio	6.80	7.10	7.28
Composition (mol fraction)			
Distillate			
$iC_4^=$	0.0646	0.0647	0.0648
$nC_4^=$	0.9354	0.9353	0.9352
EtOH	< 10 ppm	< 10 ppm	< 10 ppm
ETBE	0.0000	0.0000	0.0000
Bottoms			
$iC_4^=$	0.0008	0.0007	0.0006
$nC_4^=$	0.0206	0.0207	0.0208
EtOH	0.1426	0.1426	0.1426
ETBE	0.8360	0.8360	0.8360
Distillate flow rate (kmol/h)	86.178	86.178	86.178
Vapor boilup (kmol/h)	434.4	450.6	460.5
Reflux (kmol/h)	586.1	612.0	627.7
Reboiler duty (MW)	3.540	3.672	3.752

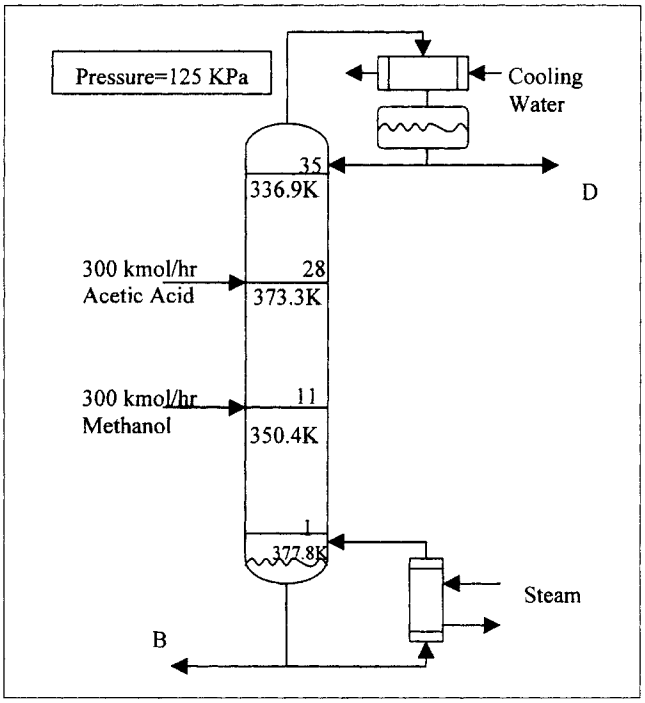

Figure 6. Methyl acetate reactive distillation column.

Eastman design uses homogeneous kinetics, which are not available. We used the heterogeneous kinetic model reported by Song et al. (1998), modified to fit the Eastman design specifications. The details of the model used are available in Al-Arfaj (1999). The modified Eastman design is shown in Figure 6.

Table 9 shows the effect of changing the number of stripping and rectifying trays in the modified Eastman design.

Table 9. Effect of Changing Fractionating Trays: Methyl Acetate System

	Low Fractionation	Base Design	High Fractionation
$N_S/N_{RX}/N_R$	**7/18/4**	**10/18/7**	**13/18/10**
Conversion	99.468	99.468	99.468
Reflux ratio	1.835	1.793	1.792
Composition (mol fraction)			
Distillate			
HOAc	0.00105	0.00143	0.00135
MeOH	0.00506	0.00355	0.00343
MeOAc	0.94900	0.94900	0.94900
H_2O	0.04489	0.04602	0.04622
Bottoms			
HOAc	0.00443	0.00402	0.00410
MeOH	0.00002	0.00168	0.00182
MeOAc	0.00000	0.00000	0.00000
H_2O	0.99555	0.99430	0.99408
Distillate flow rate (kmol/h)	314.44	314.44	314.44
Vapor boilup (kmol/h)	614.4	608.8	608.9
Reflux (kmol/h)	577.0	563.8	563.6
Reboiler duty (MW)	7.121	7.039	7.037

Conversion and product purity remain unchanged as trays are added or removed from the stripping and rectifying sections of the column. No degradation of performance results from adding more fractionation trays in the methyl acetate case as well.

Conclusion

In this article we have demonstrated that adding additional trays in a reactive distillation column does not degrade performance, provided the specified degrees of freedom are appropriately chosen. Three chemical systems have been studied.

Our future work in this area involves developing effective control structures for a variety of reactive distillation systems.

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Notation

a_B = preexponential factor for reverse reaction, kmol·s^{-1}·(kmol of holdup)$^{-1}$
a_F = preexponential factor for forward reaction, kmol·s^{-1}·(kmol of holdup)$^{-1}$
A = reactant component
B = reactant component
B = bottoms flow rate, kmol/s
C = product component
D = product component
D = distillate flow rate, kmol/s
E_B = activation energy of reverse reaction, cal/mol
E_F = activation energy of forward reaction, cal/mol
F_{0A} = fresh feed flow rate of reactant A, kmol/s
F_{0B} = fresh feed flow rate of reactant B, kmol/s
k_F = specific reaction rate of forward reaction, kmol·s^{-1}·(kmol of holdup)$^{-1}$
k_B = specific reaction rate of reverse reaction, kmol·s^{-1}·(kmol of holdup)$^{-1}$
L_n = liquid flow rate from tray n, kmol/s
M_n = liquid holdup on tray, kmol
M_{cat} = catalyst weight per tray, kg
N_R = number of rectifying trays
N_{RX} = number of reactive trays
N_S = number of stripping trays
P = total pressure, bar
P_j^S = vapor pressure of component j, bar
R = reflux flow rate, kmol/s
RR = reflux ratio
R = perfect gas law constant, cal·mol^{-1}·K^{-1}
R_C = rate of production of C, kmol of C/s
T_n = temperature in tray n, K
V_n = vapor flow rate from tray n kmol/s
V_S = vapor boilup, kmol/s
x_{nj} = composition of component j in liquid on tray n, mol fraction
y_{nj} = composition of component j in vapor on tray n, mol fraction
ΔH_v = heat of vaporization, cal/mol
λ = heat of reaction, cal/mol of C produced
α_j = relative volatility of component j

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