

Detrimental Influence of Excessive Fractionation on Reactive Distillation

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Reactive distillation has been demonstrated to reduce the capital cost and increase reactant conversion in MTBE production. These advantages are potentially transferable to the production of ETBE, TAME, and other tertiary ethers. However, the design of reactive distillation columns is complicated by interaction between phase and reaction equilibrium. Whereas in conventional distillation, an increase in fractionation is always associated with an improvement in process performance (separation of key components), the same does not necessarily apply to reactive distillation. Using the production of ETBE as an example, several reactive distillation columns were designed for various feed compositions and design philosophies. It was found that the best designs incorporated high reflux ratios with a restricted number of theoretical stages, and that increasing the number of theoretical stages could actually be detrimental to process performance.

Introduction

Ethyl *tert*-butyl ether (ETBE), methyl *tert*-butyl ether (MTBE), and several other ethers have high octane numbers (above 100) and are oxygen-rich (15–18% by weight). These properties make them suitable to replace lead-based octane enhancers and to oxygenate gasoline to meet legislative requirements. Demand for MTBE, in particular, grew strongly in the 1990s (Kirschner, 1996) and major new MTBE projects continue to be planned and built around the world (Riddle, 1996). However, ETBE has a higher octane rating, a lower volatility, and less affinity for water than MTBE and is therefore potentially a superior gasoline blending agent. ETBE production to date has been restricted (Unzelman, 1995; Cima et al., 1993), as it is currently more expensive due to the higher cost of ethanol compared with methanol, but ethanol subsidies are now helping to make it a viable alternative.

Reactive distillation was first patented for MTBE synthesis in 1980 (Smith, 1980) and was commercialized only two years later (Smith and Huddleston, 1982). The potential advantages of reactive distillation compared with the conventional process are significant: (1) reduced capital costs resulting from the combination of two unit operations into a single item of equipment; (2) increased reactant conversion by continuously recycling reactants to the reaction zone and removing prod-

ucts from the reaction zone to improve the reaction stoichiometry; and (3) increased energy efficiency through direct utilization of the heat of reaction for separation. Of the many new MTBE plants that are currently in either the planning or construction phases, most will use processes based on reactive distillation (Riddle, 1996). Similar benefits should be realizable from using reactive distillation for ETBE synthesis although this hypothesis has not yet been clearly tested.

Distillation adds value to a process by separating components with different volatilities. Increasing the separation power of a distillation column in the design phase (by adding more theoretical stages to the column) or during operation (by increasing the internal vapor and liquid flows), improves the performance of the column by increasing the purity of at least one of the distillation products, except in some azeotropic columns (Knapp and Doherty, 1994). Although this premise does not necessarily hold for reactive distillation, as change in fractionation may have an undesirable effect on the reaction by changes in the composition profile, it might be expected that a column with more theoretical stages should potentially be capable of adding more value to a process than a shorter column. Similarly, the effect of increasing the reflux ratio cannot be predicted with certainty in reactive distillation, but it might be expected that such a change would improve performance rather than impair it. Finally, it might be expected that the effect of adding stages or increasing internal flow rates would, at least, be directionally equivalent in

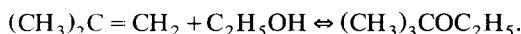
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nonreactive distillation, but this cannot necessarily be assumed for reactive distillation.

This article presents reactive distillation column designs and simulation results, obtained using Pro/II (Simulation Sciences, 1994), for ETBE production with a range of design philosophies and feed compositions, and demonstrates that increased fractionation can actually be detrimental to the process performance. This result has significant implications for the design of ETBE processes that utilize reactive distillation technology.

ETBE Production

ETBE is synthesized from ethanol and the same reactive olefin (isobutylene) that is used for MTBE production, using a protonated ion-exchange resin, such as Amberlyst 15 to catalyze the reaction:



The ETBE reaction is equilibrium limited in the industrially significant range of temperatures (40–90°C), and thermodynamically more restrictive than the MTBE reaction. The reaction is strongly exothermic and highly selective (up to 99%). The principal side reactions are the dimerization of isobutylene to form diisobutylene (DIB) and the hydration of isobutylene to form isobutanol. The latter reaction only occurs if water is allowed to enter the system. The mixture of an alcohol, an ether, olefins, and other hydrocarbons is highly nonideal and various binary azeotropes have been detected (Gmehling et al., 1994). The composition and nature of these azeotropes, and their dependence on pressure, have been described previously (Sneesby et al., 1997a).

High-purity isobutylene is generally not available within a refinery complex, nor is it necessarily desirable, as it makes control of reaction temperatures difficult (more heat is released per unit volume for high-purity feeds). However, isobutylene is present in significant concentrations in the products from steam cracking and catalytic cracking units. Typical product compositions are shown in Table 1 (Miracca, 1996; Jensen, 1996). These compositions will vary somewhat with the crude source, and also the type and activity of the catalyst used in catalytic cracking. Isobutane dehydrogenation can produce very high-purity (95%+) isobutylene, in which case dilution with another C₄ stream is desirable for etherification. The ethanol, whether sourced from renewable material (biomass) or from ethylene, must be of a high purity to minimize the formation of isobutanol that has a lower

Table 1. Typical Compositions of the Hydrocarbon Feed to Etherification Units

Component	Steam Cracking C ₄ Product	Catalytic Cracking C ₄ Product
Isobutylene	40%	15%
<i>n</i> -Butylenes	30%	35%
Butadiene	30%	—
Isobutane	—	40%
<i>n</i> -Butane	—	10%

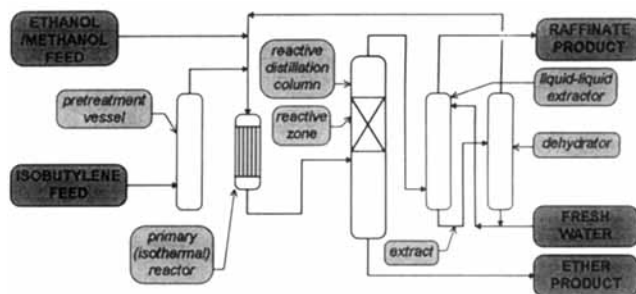


Figure 1. Ether synthesis via reactive distillation.

commercial value than ETBE and less suitable properties for gasoline blending.

The reactive distillation process for ETBE (or MTBE) production is a modification of the conventional process that consists of four main process steps (Petrochemical Processes, 1995): (1) pretreatment to remove potential catalyst poisons from the feed streams; (2) reaction (usually completed in two stages); (3) purification of the ether product; and (4) recovery of the unreacted alcohol for recycling. Where reactive distillation is used, the second (or final) reactor and the purification column are combined into a single vessel. This configuration is shown in Figure 1.

Although it is technically possible to perform all of the reaction inside a reactive distillation environment, it is not practical or economical to do so due to the difficulty of installing and removing catalyst inside the column. Retaining the first reaction stage unloads the catalyst inside the column and provides additional protection against deactivation. It also reduces the amount of heat liberated inside the column that might otherwise produce operating problems (e.g., localized flash boiling leading to premature flooding). Slightly higher conversions can also be achieved by retaining the primary reaction stage.

The reactive distillation column contains catalyst on some trays or packed sections above the feed point. Some nonreactive stages are still required above and below the reactive section to produce the necessary separation between products and reactants. The column must operate to meet two primary objectives: a high ether purity to eliminate high volatility components from the gasoline blending pool, and a high isobutylene conversion to maximize the value added by the process.

The recovery system operates by washing the distillate product with water to remove and recycle ethanol, which is sometimes a poison to downstream units. The ethanol-rich water is then distilled to separate water, which is reused in the water-wash stage, and ethanol for recycling. This process was developed for MTBE where the distillate product contains up to 10% methanol due to azeotropes that form between methanol and various C₄ components, and where there is no azeotrope between methanol and water to reduce the effectiveness of a water-wash recovery system. The same approach can still be used for ETBE, as the ratio of fresh ethanol to recovered ethanol is high, which prevents a significant concentration of water building up in the reaction stages. However, in some cases, the concentration of ethanol in the distillate product will be sufficiently low to allow the recovery system to be eliminated from the process.

Reactive Distillation Column Designs

Several reactive distillation columns have been designed for ETBE synthesis using both types of hydrocarbon feed shown in Table 1 and four different design philosophies:

1. Base-case design (30 ideal stages)
2. Maximum isobutylene conversion design
3. High ETBE purity design (minimum ethanol in the ETBE product)
4. Reduced fractionation design
5. Reduced fractionation and increased reflux design.

For each design scenario, a consistent design basis, summarized in Table 2, was used. The theoretical stages were allocated to the various column sections: 7 rectifying stages, 7 reacting stages, and 14 stripping stages. The feed stage was the uppermost stripping stage for all cases. This configuration has been previously shown to have good properties for ETBE production (Sneesby et al., 1997a). An overhead pressure of 700 kPa was selected, although the whole analysis could have been completed at a higher pressure with similar results. A constant production rate was selected to provide a comparison of the energy efficiency of the various designs.

The base-case design has similar characteristics to industrial MTBE columns but is suboptimal for ETBE production, despite the inherent similarities between the two systems. A lower reflux ratio is used for the isobutylene-lean feed case, as the higher concentration of inert C_4 components (which form the bulk of the distillate) significantly increases the column energy requirement. Traditional methods for determining the minimum reflux ratio (and subsequently for setting the actual reflux ratio using a recommended ratio of R/R_{min}) are not applicable to reactive distillation, as both product compositions must be fixed and any reaction that occurs inside the column will change the product compositions independently of fractionation. A bottoms product composition specification of 0.1 wt % total C_4 s was selected to control the Reid vapor pressure (RVP) of the product without overly constraining column operation. This is a more effective selection than the ETBE purity, as the C_4 components have a more significant effect on the RVP and blending properties of the ETBE product.

The second case considers the scenario where it is desirable to maximize the isobutylene conversion because isobutylene availability is the limiting factor is the limiting factor in production or for some other reason. Essentially, this is achieved by increasing the recycle rate of isobutylene back to the reaction zone via the reflux rate. The base-case reflux ratio was increased 50% for these cases.

The third case considers the need to minimize all contaminants (including ethanol) in the ETBE product. The presence of an azeotrope between ETBE and ethanol, and the absence of any significant azeotropes between ethanol and the various C_4 components, prevents production of ethanol-free ETBE without also losing significant ETBE in the distillate product. However, the ETBE purity can be maximized by restricting ethanol availability within the column. In each of the other cases, a small stoichiometric excess of ethanol (5%) was specified to minimize side reactions (Kitchaiya and Datta, 1995) and to maximize the isobutylene conversion. In this case, no stoichiometric excess of ethanol was used. Furthermore, the bottoms composition specification was reduced to 0.01 wt. % total C_4 s.

The final two cases consider the effects of fractionation of the reactive distillation system by the number of stages and the reflux ratio. Case 4 examines a column with only 18 theoretical stages (4 rectifying stages, 4 reacting stages, and 8 stripping stages) operating with the same reflux ratio as the other cases. The final case combines attributes from case 2 (reflux ratio increased 50%) and case 4 (only 18 stages) to assess any complementary behavior.

Column designs were completed using simulations with Pro/II (Simulation Sciences, 1994). Chemical equilibrium was assumed on all stages where catalyst is present. This assumption has previously been tested for a wide range of catalyst concentrations using detailed models of the reaction kinetics (Sneesby et al., 1997b). The ETBE reaction model of Jensen and Datta (1995) was used to provide the necessary equilibrium data. The UNIFAC model was used to predict the liquid-phase nonidealities, and all calculations were made in terms of component activities rather than concentrations. Other physical properties were predicted with the Soave-Redlich-Kwong equation of state. This combination of reaction data and physical property methods has been successfully used in previous studies and validated against experimental data for an MTBE column (Sneesby et al., 1997a,b).

The results of the design study are summarized in Table 3a (where the hydrocarbon feed is sourced from a typical steam cracking unit) and 3b (where the hydrocarbon feed is sourced from a typical catalytic cracking unit). The minimum column diameter was estimated to the nearest multiple of 150 mm (6 in.) using flooding correlations from Pro/II.

Observations on the Designs and Effects of Key Design Parameters

Increasing the reflux ratio by 50% from the base case increased the isobutylene conversion by 0.8% for an isobuty-

Table 2. Design Basis for ETBE Reactive Distillation Columns

Property	Specification
Feed composition	Equilibrium product from isothermal reactor operating at 80°C with hydrocarbon feed given in Table 1 and 5% stoichiometric excess of ethanol (except case 3)
Theoretical stages	7 rectifying, 7 reacting, and 14 stripping (except cases 4 and 5)
Feed stage	Uppermost stripping stage
Overhead pressure	700 kPa
ETBE product composition	0.1% total C_4 (except case 3)
Reflux rate	1.20 for isobutylene-rich feeds or 0.80 for isobutylene-lean feeds (except cases 2 and 5)
Production rate	5,000 kg/h of ETBE

Table 3. ETBE Reactive Distillation Column Designs

	<i>a. Isobutylene-Rich Feed</i>				
	Design 1 Base Case	Design 2 High Reflux	Design 3 High Purity	Design 4 Reduced Fract.	Design 5 High Reflux and Reduced Fract.
Reactor feed rate (kg/h)	10,310	10,220	10,310	10,150	9,760
Overall isobutylene conversion	89.7%	90.5%	88.6%	91.1%	94.7%
Bottoms composition (wt. %)	91.3% ETBE, 7.6% EtOH, 1.0% DIB, 0.1% C ₄ s	91.2% ETBE, 7.1% EtOH, 1.6% DIB, 0.1% C ₄ s	92.8% ETBE, 5.9% EtOH, 1.3% DIB, 0.01% C ₄ s	92.5% ETBE, 6.8% EtOH, 0.6% DIB, 0.1% C ₄ s	94.1% ETBE, 5.1% EtOH, 0.7% DIB, 0.1% C ₄ s
Distillate composition (wt. %)	5.9% <i>i</i> But, 94.1% other C ₄ s, 3 ppm EtOH	4.9% <i>i</i> But, 95.1% other C ₄ s, 1 ppm EtOH	6.4% <i>i</i> But, 93.6% other C ₄ s, 2 ppm EtOH	5.6% <i>i</i> But, 94.3% other C ₄ s, 0.06% EtOH	5.7% <i>i</i> But, 94.3% other C ₄ s, 90 ppm EtOH, 1 ppm ETBE
Reboiler duty (MW)	1.14	1.40	1.17	1.12	1.31
No. of theoretical stages (rectifying/reactive/stripping)	7/7/14	7/7/14	7/7/14	4/4/8	4/4/8
Approx. column dia. (mm)	900	900	900	900	900
<i>b. Isobutylene-Lean Feed</i>					
Reactor feed rate (kg/h)	22,450	22,220	22,750	21,650	21,390
Overall isobutylene conversion	94.4%	95.5%	92.7%	98.0%	99.2%
Bottoms composition (wt%)	94.0% ETBE, 5.1% EtOH, 0.8% DIB, 0.1% C ₄ s	94.3% ETBE, 4.7% EtOH, 0.9% DIB, 0.1% C ₄ s	95.3% ETBE, 3.7% EtOH, 0.9% DIB, 0.01% C ₄ s	97.1% ETBE, 2.2% EtOH, 0.7% DIB, 0.1% C ₄ s	97.6% ETBE, 1.6% EtOH, 0.7% DIB, 0.1% C ₄ s
Distillate Composition (wt%)	0.85% <i>i</i> But, 99.1% other C ₄ s, 0.04% EtOH	0.66% <i>i</i> But, 99.3% other C ₄ s, 0.02% EtOH	1.11% <i>i</i> But, 98.9% other C ₄ s, 0.02% EtOH	0.31% <i>i</i> But, 99.2% other C ₄ s, 0.47% EtOH	0.10% <i>i</i> But, 99.4% other C ₄ s, 0.46% EtOH, 1 ppm ETBE
Reboiler duty (MW)	2.75	3.40	2.82	2.66	3.29
Number of theoretical stages (rectifying/reactive/stripping)	7/7/14	7/7/14	7/7/14	4/4/8	4/4/8
Approximate column diameter (mm)	1,500	1,650	1,500	1,650	1,500

lene-rich feed and 1.1% for an isobutylene-lean feed. In both cases, the ETBE purity was essentially unchanged. Such a result could be anticipated by considering that reflux acts similarly to recycle in the case of reactive distillation. The effect on fractionation is only minor, as the base-case reflux ratio is already relatively high. A similar result might be expected for nonreactive distillation for a column already operating at a nearly optimal reflux ratio.

The changes implemented in Design 3 were effective in increasing the ether product purity, although an increase of only 1.2–1.3% was attained. The operating changes have had an unfavorable effect on the reaction conditions, as the isobutylene conversion decreased for both feed types. This highlights the significant interaction that occurs between the phase and reaction equilibria in reactive distillation.

The effect of reduced fractionation (Design 4) is interesting and nonintuitive. *The ETBE purity was increased significantly and the overall column performance was enhanced for both types of feed when the number of theoretical stages was reduced from 30 to 18.* The distillate product became less pure (the ethanol concentration increases in both cases), but this has a favorable effect on the reaction-zone conditions, and more ETBE is produced. In nonreactive distillation, the effect of increasing reflux ratio and increasing the number of stages should be directionally equivalent. In this example of reactive distillation, the reverse is true. This is confirmed by the final design case, which combines the increased reflux ratio used in Design 2 with the reduced fractionation used in Design 4. The result is a very high ETBE purity and a very high isobutylene conversion, attained simultaneously. Indeed,

Design 5 is clearly preferred to any of the other designs, particularly where an isobutylene-lean feed is used since a conversion of greater than 99% is combined with a product purity of nearly 98%. Interestingly, these results cannot be reproduced in a column with 30 theoretical stages at any reflux ratio or combination of product specifications.

Although the benefits of reducing fractionation have been demonstrated in this case, the change resulted in a higher ethanol concentration in the distillate. This is potentially harmful if there is no ethanol recovery equipment downstream of the reactive distillation column and ethanol is an unwanted contaminant or poison in a downstream process. As indicated previously, this is possible for ETBE production since the ethanol concentration in the distillate is typically very low, especially for isobutylene-rich feeds. However, any undesirable effects of reduced fractionation can be offset with a further increase in the reflux ratio, which will lower the ethanol in the distillate concentration.

Fractionation Effects in Other Columns

To confirm the result that fractionation can be detrimental in the design of reactive distillation columns, a third series of designs was completed. A hydrocarbon stream containing 25% isobutylene and 75% *n*-butylene was combined with a stoichiometric amount of ethanol and reacted to 70% isobutylene conversion to create a suitable feed for a series of reactive columns with varying numbers of stages. The same distribution of stages (constant ratio of rectifying:reac-

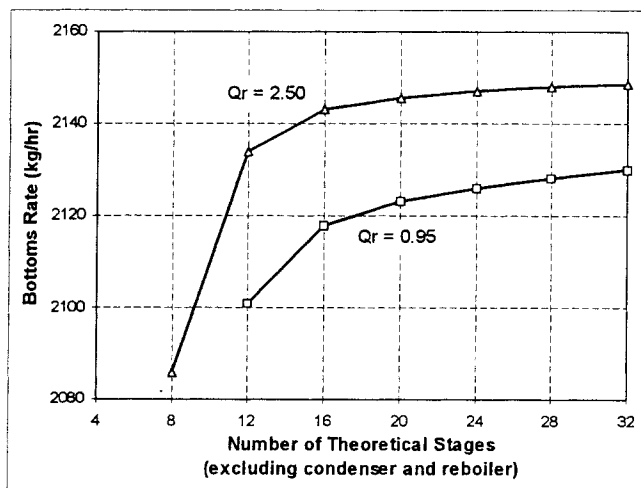


Figure 2. Effect of increasing fractionation on yield in nonreactive columns.

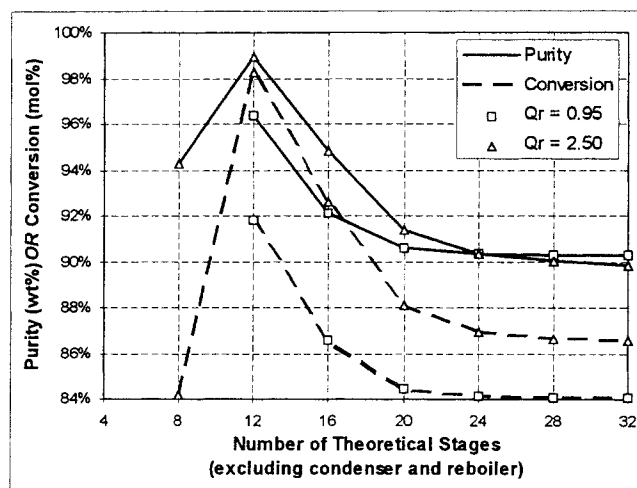


Figure 4. Effect of increasing fractionation on purity and conversion in reactive columns.

tive:stripping stages), product specification (0.1% C_4 in the bottoms), and reboiler duty were specified in each column.

The intuitive effect of increasing fractionation with a constant composition specification is to increase the yield of the product under control. In this case, the bottoms rate should increase with the number of stages in the column. This behavior is exactly seen in a nonreactive column that is otherwise identical to the column described earlier (i.e., the reactive stages are simply exchanged for nonreactive stages). This is shown in Figure 2 for two values of the reboiler duty (0.95 and 2.50 MW per 100 kmol/h of C_4 feed).

The reactive columns show a completely different response where increasing the fractionation often reduces the bottoms product yield. This is shown in Figure 3, which is exactly analogous to Figure 2. Figure 4 shows how the ETBE concentration and the isobutylene conversion vary with the total number of stages. As indicated previously, the interaction between the phase and reaction equilibrium is such that the isobutylene conversion (and hence the ETBE purity) is maxi-

mized when the column internal compositions are optimized. This occurs at an intermediate level of fractionation rather than an extreme.

Reactive distillation column designs were also completed for the MTBE system, using identical feed compositions and design basis (cf. Tables 1 and 2). Interestingly, somewhat different results were observed. The benefit of increasing the reflux ratio was still evident (the predominant effect of this is to recycle reactive components), but no advantage was found from reducing the fractionation from the base case of 30 ideal stages. The difference with the ETBE system lies in the presence of several binary low-boiling azeotropes between methanol and various C_4 components. Provided the internal ratio of methanol to C_4 is lower than the azeotropic composition, the effect of increasing the stripping section separation is to recycle methanol to the reactive section and promote further reaction. Unfortunately, a similarly useful azeotrope does not exist at the top of the column, so the rectifying separation must again be optimized. As with the ETBE system, the reactive distillation of MTBE is infeasible with perfect separation (infinite stages and infinite reflux).

Multiple steady states are possible in both ETBE and MTBE reactive distillation columns, but their presence is independent of the fractionation effects described here. Multiplicities were detected in some of the columns described before, but, when multiple solutions existed, only the high conversion solution was considered and the behavior of those columns was fully consistent with the others.

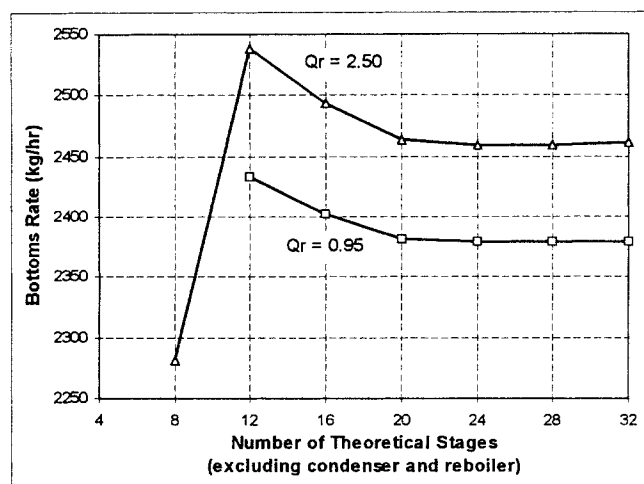


Figure 3. Effect of increasing fractionation on yield in reactive columns.

Conclusions

Reactive distillation column designs for ETBE production were completed for a range of design bases and two typical feed compositions. Excessive fractionation was found to have a detrimental influence on the overall column performance. Both higher ETBE purity and higher isobutylene conversion were possible in a column with significantly fewer theoretical stages than the base case. However, increasing the reflux ratio proved beneficial in all cases.

This nonintuitive result is explained by the interaction of phase and chemical equilibria that occur in reactive distillation: in order to maximize ETBE purity, reaction zone conditions must be optimized to favor the synthesis reaction over the decomposition reaction, and the optimal conditions result from a composition profile with only limited separation between reacting components. This result is not present in MTBE reactive distillation due to the effect of azeotropes between methanol and various C₄ components, which allows increased fractionation to have a positive effect on the reaction zone conditions. In general, however, it may be said that the design of reactive distillation columns is not only a compromise between performance and energy consumption (as is the case with conventional distillation) but an optimization of a wide range of interacting parameters.

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