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Multiple Solutions in Reactive Distillation for Methyl *tert*-Butyl Ether Synthesis

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A reactive distillation column for the synthesis of methyl *tert*-butyl ether (MTBE) is simulated using a steady-state equilibrium stage model. For identical column and feed specifications, two distinctly different composition profiles are obtained, which correspond to high and low conversion of isobutene. With the aid of residue curve maps for simultaneous physical and chemical equilibrium, it is shown that the high- and low-conversion steady-state composition profiles obtained in the column simulations correspond to residue curves which have their starting points in distinctly different composition regions.

Introduction

A reactive distillation column typically consists of three zones (see Figure 1). The *reactive distillation zone* contains catalyst in the form of structured packing material. Separation of the inerts takes place in the *rectification section* of the column, and the purification of the product takes place in the *stripping section*. Reactive distillation is an attractive processing scheme for an equilibrium limited reaction such as methyl *tert*-butyl ether (MTBE) synthesis; due to in situ removal of product from the reaction zone the equilibrium is shifted toward the right and it is therefore possible to realize high conversion (DeGarmo *et al.*, 1992). MTBE is produced by reaction of isobutene and methanol; the liquid-phase reaction is catalyzed by an acidic catalyst, for example Amberlyst 15. A typical mixed butenes feed for MTBE synthesis consists of about 40% isobutene and 60% *n*-butene, which is inert and does not react.

In the MTBE synthesis process it is desirable to obtain a bottom product containing high-purity MTBE and a distillate containing high-purity *n*-butene. High isobutene conversion is desired to produce a distillate containing only a minute amount of isobutene. The top product may contain some methanol. In a design study for MTBE using the reactive distillation concept, Nijhuis *et al.* (1992) detected steady-state multiplicity of column profiles akin to that observed by Rovaglio and Doherty (1990) for heterogeneous azeotropic distillation. The recent review of Doherty and Buzad (1992) hints at the possibility of multiple steady states in reactive distillation systems. It is the objective of the present paper to confirm the possibility of multiple solutions for MTBE synthesis and offer a physical reason for this phenomenon. A further objective is to suggest optimum operating conditions and column configuration for MTBE synthesis.

Reactive Distillation Simulations

The simulation of the MTBE column is carried out using the rigorous distillation model RADFRAC from the flowsheet simulator Aspen Plus (see Venkataraman *et al.* (1990)). In the simulations a property set Sysop11 that contains UNIQUAC/Redlich–Kwong is used. The reaction kinetics is obtained from literature (see Rehfinger and Hoffmann (1990)). Since the system is highly nonideal, reaction kinetics is expressed in terms of activities. The binary UNIQUAC parameters used in the simulations were those published by Rehfinger and Hoffmann (1990).

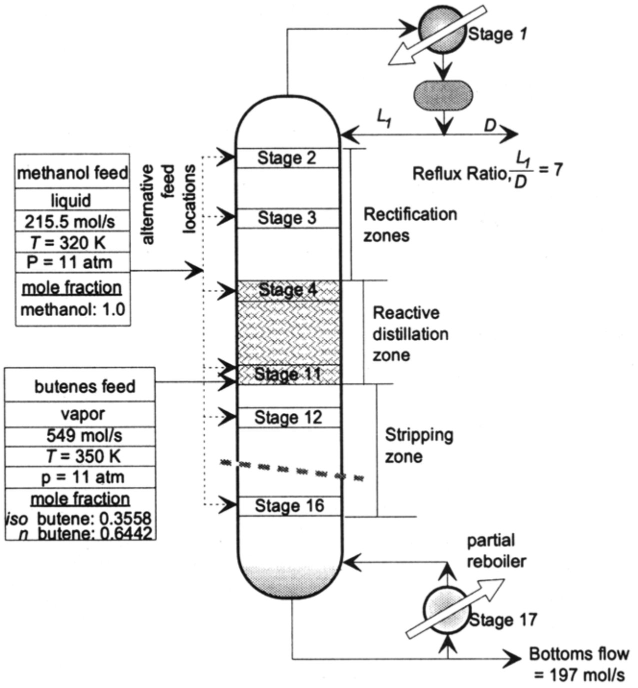

Figure 1. Reactive distillation column configuration and feed specifications.

The column configuration chosen for the simulations is shown in Figure 1. The total number of stages is 17, including a total condenser and a partial reboiler; the column pressure is 11 atm. Reactive stages are located in the middle of the column, stage 4 down to and including stage 11 (the numbering of the stages is top downward). The column has two feed streams: a methanol feed and a mixed butenes feed; a small stoichiometric excess of methanol is used. The methanol feed stage location is varied in the simulations between stage 2 and stage 16. The mixed butenes feed, to stage 11, contains a mixture of isobutene and *n*-butene. On a stage in the reactive zone 1000 kg of catalyst is introduced and the reaction rates are calculated assuming a pseudohomogenous model (i.e., neglecting intracatalyst diffusion limitations). The reflux ratio is set to 7, and the bottom flow rate is set to 197 mol/s.

A series of simulation runs were carried out with varying methanol feed stage location; the methanol feed is moved sequentially down the column from stage 2 to stage 16 and

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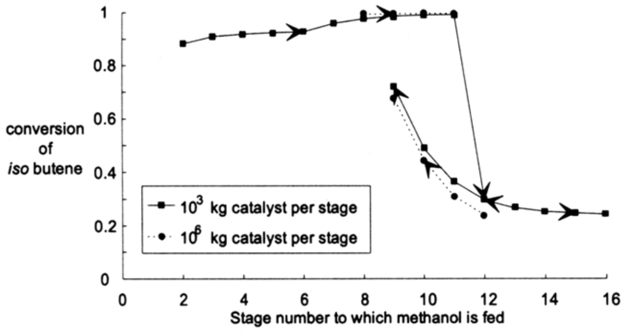

Figure 2. Conversion of isobutene as a function of methanol feed stage location.

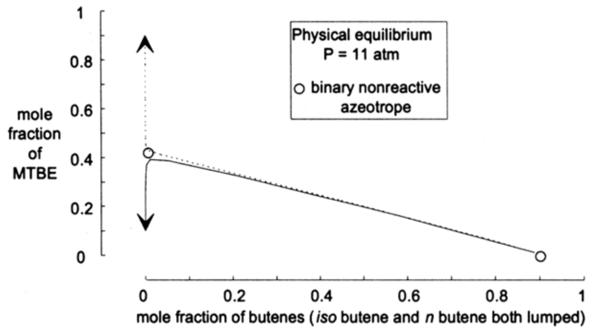

Figure 3. Limiting residue curves for physical equilibrium. The mole fractions of isobutene and n-butene are lumped.

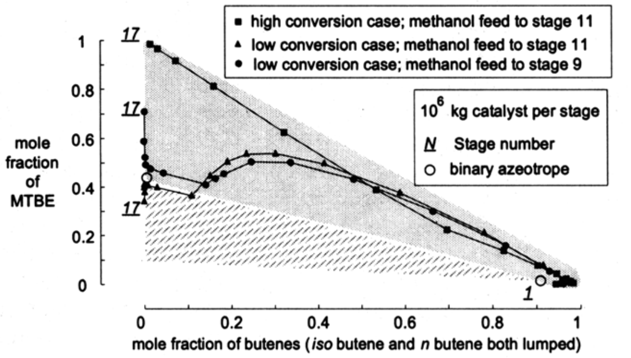

Figure 4. Column composition trajectories for high and low conversion cases.

up again. Since the system is highly nonideal, it is difficult to obtain convergence. Once a run is completed successfully, different cases are generated by slightly altering the specifications and initiating the calculations using the previously obtained, converged, results.

Multiple Solutions

Moving the methanol feed down the column from stage 2 to stage 11 gives a series of solutions that correspond to high (90%+) conversion. When the feed is moved one stage further, i.e., to stage 12, a sharp decrease in conversion is observed; see Figure 2. A series of low-conversion solutions is found moving the methanol feed from stage 12 to stage 16. Starting at stage 16, the methanol feed is moved upward. Until stage 12 the solutions for the up- and down-going sequences are identical. Continuing the up-going sequence beyond stage 12 does not give the expected jump back to the high-conversion level, but a different set of solutions is found. Thus a set of low-conversion solutions is found for stage 11 to stage 9. When the feed is added at stage 8, no solution is found; see Figure 2.

The above described simulation is repeated using a column with twice as many stages and a Murphree stage efficiency of 0.5. The total amount of catalyst is kept the same and the butenes feed is added at stage 22. The same qualitative results are found in this case. To find an explanation for the multple solutions, several checks and additional calculations are carried out.

Crossing of Nonreactive Distillation Boundaries

Nonreactive distillation boundaries can be crossed by means of chemical reaction, when after crossing a nonreactive distillation boundary reactive trays are followed by ordinary distillation trays; in such cases the column profile develops in a different direction (Doherty and Buzad, 1992; Rev, 1992). This can give rise to different steady-state solutions. Since the two butenes are very similar, in comparison to the other two components, they can be lumped into one component and so composition profiles can be presented in a ternary diagram. First the distillation boundaries for the ternary system will be elucidated. The binary pairs of the system butene–MTBE–methanol have the following characteristics: butene–MTBE, ideal; butene–methanol, minimum boiling azeotrope; MTBE–methanol, minimum boiling azeotrope. Despite the fact that two binary pairs form minimum azeotropes, multicomponent azeotropes are not found for this system (Barbosa and Doherty, 1988). The ternary system is split in two areas, one region containing residue curves ending up in pure methanol and the other region containing residue curves ending up in pure MTBE. All residue curves start at the binary azeotrope butene–methanol; the two limiting residue curves move in the direction of the methanol–MTBE azeotrope. Hereafter the residue curves bend either in the direction of pure methanol or in the direction of pure MTBE; see Figure 3. Similar results for this system were obtained by Barbosa and Doherty (1988) albeit at a different pressure of 1 atm.

For all column profiles corresponding to the high-conversion branch of the hysterisis curve (Figure 2), the nonreactive distillation boundaries are not crossed. This is illustrated in Figure 4 for one typical run in which the methanol feed is to stage 11 (the tray compositions are indicated by squares). For the low-conversion branch of the hysterisis curve, crossing of the nonreactive distillation boundary does occur; this is illustrated in Figure 4 for the case in which methanol is fed to stage 11, indicated by triangles. It can be seen in Figure 4 that two quite distinct, qualitatively different, column (liquid) composition profiles are obtained for identical column configurations. In one case the nonreactive distillation boundary is crossed (low-conversion case), and in the other case the nonreactive distillation boundary is not crossed (high-conversion cases). However, the multiplicity of steady states cannot be attributed to the crossing of nonreactive distillation boundaries alone. This is because for some low-conversion solutions, when the methanol is fed to stages 9 and 10, crossing of the nonreactive distillation boundary does not occur. This is exemplified in Figure 4 by the column composition profiles obtained when the methanol is fed to stage 9, indicated by circles.

Since the series of low-conversion solutions does not consist entirely of composition profiles that cross the nonreactive distillation boundary, the multiplicity is not explained by crossing of nonreactive distillation boundaries.

Multiplicity of Steady-State Solutions in a CSTR

Rehfinger and Hoffmann (1990) showed that in certain cases an isothermal CSTR has multiple solutions. Are the multiple solutions in the reactive distillation column caused by this kind of ignition-extinguishing behavior? In a reactive distillation column the rate of reaction on a stage influences the column profile; consequently a reactive stage, unlike a CSTR, alters its own feed rate and composition. This makes a comparison with a CSTR impossible. Another way to check whether CSTR arguments are responsible for multiplicity of steady-state solutions is to enforce chemical equilibrium by employing a large excess of catalyst. Operation of a CSTR at equilibrium precludes the occurrence of multiple solutions.

The simulations are repeated in exactly the same way as described previously, but before changing the location of the methanol feed the amount of catalyst on a stage is varied. Starting with 10^3 kg of catalyst on a stage, the weight is increased, in a few steps, to 10^6 kg; the reverse procedure is followed back to 10^3 kg of catalyst. Before the methanol feed is moved to the next stage, it is checked that the original solution is retrieved; this is true in all cases. The composition profiles for the new case are identical to the ones obtained in the 10^3 kg of catalyst case; no changes are observed with respect to crossing of the nonreactive distillation boundaries discussed above. A plot of the conversions retrieved fro this new case is also shown in Figure 2 by the dotted lines. Clearly the character of the problem is not affected by increasing the amount of catalyst. For the series of high conversion, conversion increases when catalyst weight is increased. On the other hand, for the series of low-conversion "solutions" *increasing* the catalyst loading per stage from 10^3 kg to 10^6 kg it is observed that the conversion of isobutene *decreases* still further, a quite remarkable result.

Multiple solutions cannot be explained assuming a jump to another solution as described by Rehfinger and Hoffmann (1990) for an isothermal CSTR, because multiple solutions still persist when 10^6 kg of catalyst is added on each reactive stage; the reaction in this case is equilibrium limited. An explanation for the multiple solutions cannot involve a dependency on the reaction rate expression as do the CSTR arguments of Rehfinger and Hoffmann (1990).

Simultaneous Physical and Chemical Equilibrium

In the above it is seen that even with "forced" chemical equilibrium (by using large excess of catalyst) multiple solutions still persist. Can the cause of multiple solutions be found in *simultaneous* physical and chemical equilibrium? Residue curve maps for simultaneous physical and chemical equilibrium were generated much along the lines suggested by Barbosa and Doherty (1988). Note that in the case of simultaneous physical and chemical equilibrium the two butenes can not be lumped, since one is an inert and the other is a reactant. All residue curves finally end up at the same composition but there are two fundamentally different types of residue trajectories; see Figure 5. In the first type the residue trajectories emanate from regions rich in isobutene. In the second type the residue trajectories have their starting point near the n-butene–methanol azeotrope. The residue curve maps in Figure 5 can now be used to understand the multiplicity of column composition profiles.

The column composition profiles corresponding to high- and low-conversion cases for the reactive distillation column with the methanol feed on stage 11 are shown in Figure 6. The reactive stages of the high-conversion composition profile follow a path that is similar to a residue curve starting in the vicinity of the n-butene–methanol azeotrope. In sharp contrast to the high-conversion case, in the low-conversion case the composition trajectory followed has its starting point in the vicinity of pure isobutene. The two composition profiles portrayed in Figure 6 are characteristic of all observed composition profiles for the high- and low-conversion cases found in the simulations.

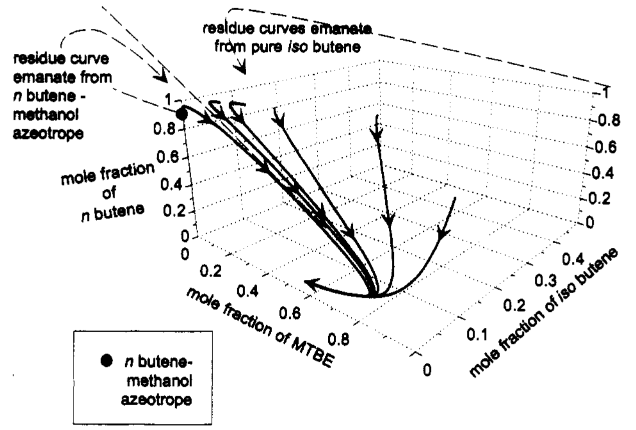

Figure 5. Residue curves for simultaneous physical and chemical equilibrium.

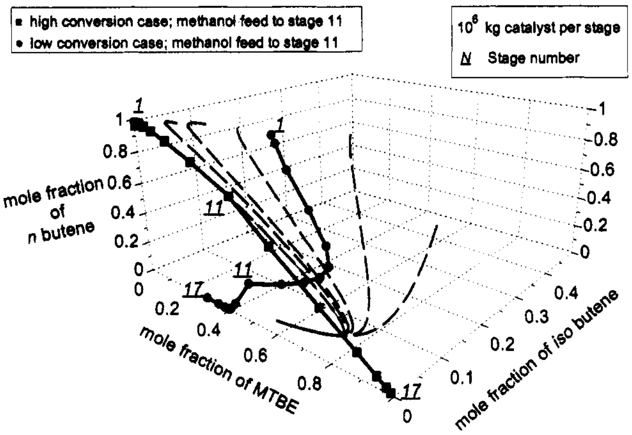

Figure 6. Column composition trajectories superimposed on residue curve maps.

An extra check was carried out. Starting with the liquid-phase compositions at stage 4, the reactive stage closest to the top of the column, "reverse" residue curve maps were generated, adding vapor to the residue. This was done for all column configurations possessing multiple solutions, using the 10^6 kg of catalyst case. For high conversion all "reverse" residue curves move in the direction of the n-butene–methanol azeotrope; for low conversion all "reverse" residue curves move toward pure isobutene.

It is concluded that multiple solutions are found because the column profile can develop along two distinctively different paths, which correspond to two different kinds of residue curves for simultaneous physical and chemical equilibrium.

Discussion

A high purity of MTBE in the bottom product can be obtained by adding nonreactive stages at the bottom of the distillation column. The effect of nonreactive stages is best explained by Figures 3 and 4. It is necessary to start on the side of the simple distillation boundary that contains the residue curves going in the direction of pure MTBE; otherwise the composition profile will develop in the direction of methanol.

If the simulations were carried out without the inert, n-butene, the composition space in Figures 5 and 6 degenerates to a plane. In this case only one type of residue curve for simultaneous physical and chemical equilibrium is found, so multiple solutions cannot be realized. The inerts play a key role in the design of a reactive distillation column. If the concentration of n-butene in the column is maintained at sufficiently high level, we can ensure that the column operation would be dictated by the residue curve emanating from the n-butene–methanol azeotrope.

Conclusions

For a reactive distillation column multiple solutions are found; the same column configuration can give two different conversions, for example 36% or 99% isobutene conversion.

Nonreactive distillation boundaries are crossed; this gives composition profiles which develop in opposite directions, but this does not explain the multiple solutions.

Multiple solutions are also found when reaction on a tray is equilibrium controlled; there is no dependency on the reaction rate expression.

Composition profiles of different kinds of solutions follow residue curves for simultaneous physical and chemical equilibrium, which have their starting point in two different regions. High conversion corresponds to residue curves starting near the n-butene–methanol azeotrope; low conversion corresponds to residue curves starting in pure isobutene.

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