

Bifurcation Study of Kinetic Effects in Reactive Distillation

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Simple distillation with multiple chemical reactions of arbitrary stoichiometry is described, with emphasis on effects of chemical kinetics. For low and high Damköhler number, the lightest and heaviest boiling components or azeotropes are known or can be found by known methods. In those limits, the products from a distillation can be anticipated and feasible separation structures can be identified. Feasible structures in these cases are not the same, however, and there are one or more transitions so that different structures can appear for different ranges of the Damköhler number. The transition points correspond to bifurcations, and using bifurcation analysis and continuation methods a systematic method that represents these changes was developed. The practical implication is that the feasibility and product purities for a reactive distillation may depend on production rate, catalyst level, and liquid holdup. The approach is illustrated for the production of methyl-tert-butyl ether (MTBE), where a critical Damköhler number for the disappearance of a distillation boundary is found. The influence of pressure on byproduct reactions in methyl acetate synthesis is also studied. A study of the synthesis of isopropyl acetate illustrates how the bifurcation method captures the essential kinetic effects in reactive distillation, including a critical Damköhler for the birth of a reactive azeotrope.

Introduction

Reactive distillation has the demonstrated potential to lower costs and reduce energy consumption and waste production (e.g., Agreda et al., 1990; Grosser et al., 1987; Smith, 1981, 1990). It is not useful in every situation, however, and more systematic methods for deciding feasibility would be useful. One tool for the synthesis and analysis of both nonreactive and reactive distillation systems is the residue curve map (RCM), which is the phase plane of the liquid compositions in an isobaric open evaporation. The simple distillation experiment is easy to perform and easy to analyze. For nonreactive systems, the results are topologically equivalent to the composition profiles in a continuous column at infinite reflux and can thus give feasibility information for continuous columns. For equilibrium reactive distillation, the simple distillation equations can be simplified using transformations of the compositions that behave in many ways like their nonre-

active counterparts (Barbosa and Doherty, 1988; Ung and Doherty, 1995).

Such transformations are not known for kinetically controlled reactive distillation. Of course, the kinetics are important in many systems, when the reaction rate may not be high enough or the liquid holdup may not be large enough to allow a close approach to reaction equilibrium. For instance, the equilibrium analysis alone is insufficient for systems with multiple reactions in which the main product is an intermediate that may react further with other reactants and/or products because the selectivity is of key concern for such chemistries. Kinetically controlled reactive distillation (and hence the structure of the RCM) may be quite different from nonreactive and equilibrium reactive systems.

A key parameter in the study of kinetically controlled reactive distillation systems is a Damköhler number (Da), the ratio of a characteristic residence time to a characteristic reaction time (Damköhler, 1939; Venimadhavan et al., 1994). A small Da implies a nonreactive system while a large Da im-

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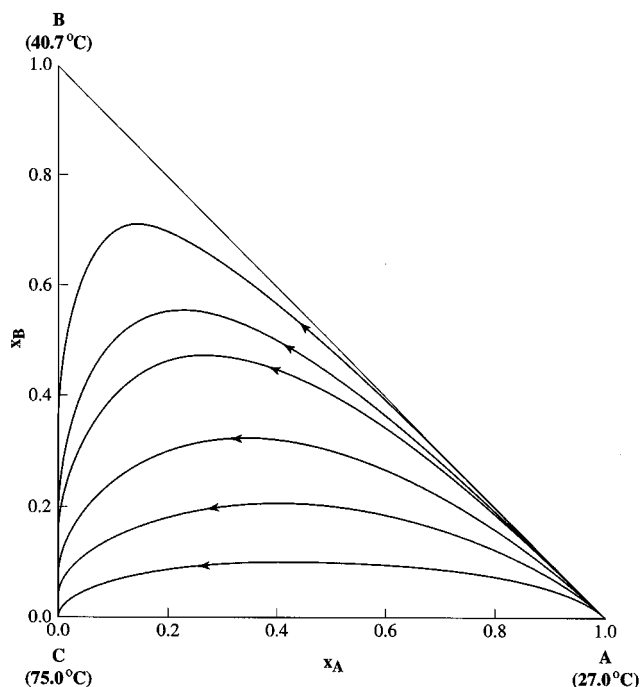


Figure 1. Residue curve map for the hypothetical ternary mixture of A, B and C with no chemical reaction ($Da = 0$).

A is the lightest component, B is the intermediate, and C is the heaviest.

plies reaction equilibrium. The lightest and heaviest boiling components or azeotropes are known or can be found by known methods in these limits, the products from a distillation can be anticipated, and feasible separation structures, that is, arrangements of columns and their products can be identified. However, the feasible structures in these limiting cases are generally different, so there are one or more transitions, and different structures can appear for different ranges of the Damköhler number. The practical implication is that the feasibility and product purities for a reactive distillation may depend on production rate, catalyst level, and liquid holdup.

The primary purpose of this article is to assess the feasibility of reactive distillation in a systematic and comprehensive way. The method exploits a bifurcation analysis in order to classify all of the various different feasible splits as a function of the Damköhler number.

Table 1. Antoine Constants and Normal Boiling Points for the A, B, C System*

Component	Normal Boiling Point (°C)	Coefficient		
		<i>a</i>	<i>b</i>	<i>c</i>
A	27.0	23.1962	-3,502.77	0.0
B	40.7	22.6867	-3,502.77	0.0
C	75.0	21.5872	-3,502.77	0.0

*The Antoine equation is

$$\ln(P^{\text{sat}}) = a + \frac{b}{T + c}, \quad \text{with } P^{\text{sat}} \text{ in Pa, and } T \text{ in K.}$$

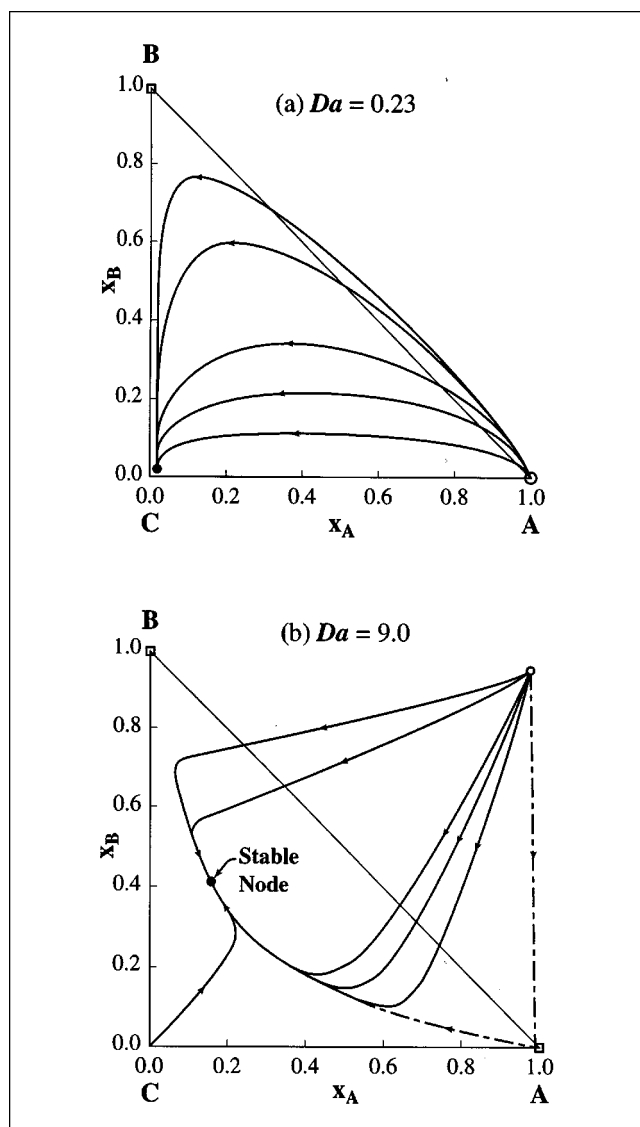


Figure 2. Residue curve map for the hypothetical ternary mixture of A, B and C with the chemical reaction $A + B \rightleftharpoons C$, $K_{\text{eq}} = 5$.

(a) Small and (b) large Damköhler number.

Figure 1 shows the residue curve map for a hypothetical mixture of A, B, and C without reaction ($Da = 0$); Raoult's Law was used to model the vapor-liquid equilibrium, with the Antoine parameters in Table 1. In the RCM all of the trajectories start at pure A, which is the lightest boiler (unstable node), go via the intermediate boiler B (saddle), and end at the heavy boiler C (stable node). As Da is increased, the trajectories no longer end near C (see, e.g., Figure 2b). This is because some of the C will react to give a three-component mixture, so the stable node occurs inside the triangle. Thus, a column without a nonreactive zone cannot produce component C in high purity.

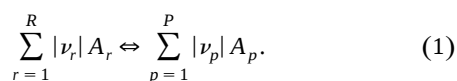
There is a qualitative difference between Figures 1 and 2b, and for systems with two degrees of freedom it is possible to find and classify such differences by inspecting the RCM at different values of Da . However, a more systematic and gen-

eral approach that applies to cases with more degrees of freedom is needed. In this article we describe a bifurcation analysis to accomplish this and illustrate the method on four examples. These are:

1. The hypothetical A , B , C mixture previously introduced.
2. The chemical synthesis of methyl-*tert*-butyl ether (MTBE) from isobutene and methanol.
3. The esterification of acetic acid with methanol to produce methyl acetate, including a side reaction of the dehydration of methanol to dimethyl ether (DME) and water.
4. The reaction of acetic acid with isopropanol to give isopropyl-acetate and water. This illustrates the fact that we can make qualitative predictions of the system behavior even when a detailed kinetic model is lacking, as is often the case when designing experiments.

Bifurcation Analysis of Simple Distillation

For a system with a single chemical reaction of the form



The simple distillation equations are

$$\frac{dx_i}{d\xi} = x_i - y_i + Da \frac{H}{H_0} \frac{V_0}{V} (\nu_i - \nu_T x_i) \Re \quad (2)$$

$i = 1, \dots, (R + P - 1),$

where Da is the Damköhler number defined here as

$$Da = \frac{H_0/V_0}{1/k_{f,\text{ref}}} \quad (3)$$

and

$$\Re = \frac{r}{k_{f,\text{ref}}}. \quad (4)$$

Here, x_i are the liquid-phase mole fractions; y_i are the corresponding vapor-phase mole fractions; ξ is the dimensionless “warped” time, which is related to the clock time t from

$$d\xi = \frac{V}{H} dt, \quad (5)$$

where H and H_0 are the instantaneous and initial liquid holdups in the still in moles; V and V_0 are the instantaneous and initial vapor rates from the still; r is the rate of reaction per mole of mixture; $k_{f,\text{ref}}$ is the forward reaction rate constant evaluated at a reference temperature; ν_i is the stoichiometric coefficient of component i in the reaction; and ν_T is the sum of the stoichiometric coefficients for the reaction. The dimensions of r , k_f , and $k_{f,\text{ref}}$ are inverse time.

Da can have values from zero (no reaction) to infinity (equilibrium reaction). For Da between zero and unity, the

residence time is less than the reaction time, and for all values of Da larger than unity, the residence time is greater than the reaction time. It is convenient to introduce a new dimensionless parameter D as

$$D = \frac{Da}{1 + Da}, \quad (6)$$

where D varies from zero for the case of no reaction, to unity in the limit of reaction equilibrium. Moreover, D is more symmetric; for D between zero and one-half, the residence time is less than the reaction time, while for values of D between one-half and unity, the residence time is greater than the reaction time.

A more convenient rescaled warped time is

$$d\zeta = (1 + Da) d\xi. \quad (7)$$

For a specific vapor rate policy of $H \propto V$ (Venimadhavan et al., 1994, 1999), the governing equation for simple distillation becomes

$$\frac{dx_i}{d\zeta} = (1 - D)(x_i - y_i) + D(\nu_i + \nu_T x_i) \Re \quad (8)$$

$i = 1, \dots, (R + P - 1).$

The structure of the RCM is determined by the position of the singular points (nodes and saddles) of Eq. 8, which depend on the value of D . Note that the heating policy required to achieve $H \propto V$ can be calculated separately from an energy balance. If this heating policy is not implemented, the structure of the fixed points and the residue curves will be different (see, e.g., Venimadhavan et al., 1994).

A systematic way to study these changes is a bifurcation analysis of the steady-state solutions of Eq. 8 as a function of D . The starting points for the analysis are the singular points for the nonreactive mixture, which are the pure components and the nonreactive azeotropes at $D = 0$. Fortunately, there is a robust homotopy continuation method that can calculate all of the nonreactive azeotropes of a mixture given the pure components and a VLE model (Fidkowski et al., 1993). Therefore, we can find all of the starting points for the bifurcation analysis. Many quantities can be used to represent the solutions; we use the mixture boiling temperature as a function of D . The branches were calculated using the pseudoarc-length continuation method in AUTO (Doedel, 1986). We now apply this technique to four examples mentioned earlier.

Simple Hypothetical Example

The first example is the hypothetical mixture of three components A , B , and C (A is the lightest, B is the intermediate boiler, and C is the heavy boiler) with a reaction of the form:



We assume that the reaction equilibrium constant is independent of temperature and has a constant value of $K_{\text{eq}} = 5$.

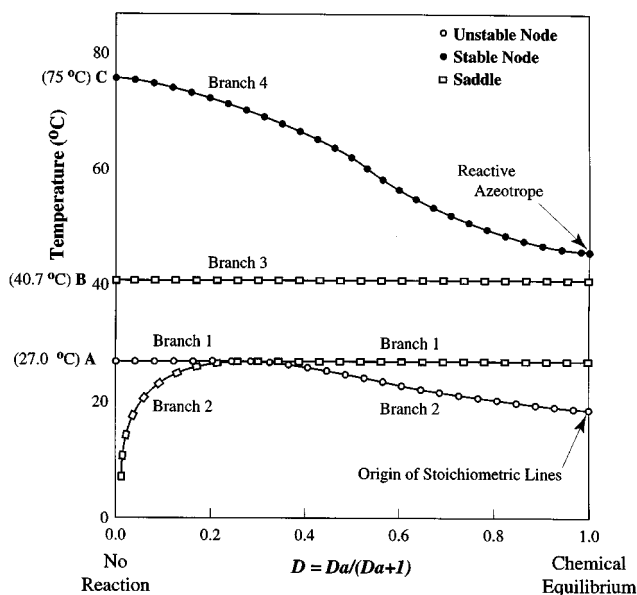


Figure 3. Bifurcation diagram for the hypothetical ternary mixture of A, B and C with the chemical reaction $A + B \rightleftharpoons C$, $K_{eq} = 5$ at 1 atm.

Raoult's law is used to describe the VLE (see Table 1 for the Antoine parameters), and the rate of reaction per mole of mixture is given by

$$r = k_f \left(x_A x_B - \frac{x_C}{K_{eq}} \right). \quad (10)$$

For this example we imagine that the forward reaction rate constant is independent of temperature so that $k_f/k_{f,ref} = 1$.

At $D = 0$, there are three singular points corresponding to the three pure components. These are the starting points for the bifurcation diagram shown in Figure 3. As D is increased, the stable node moves inside the composition triangle (see Figure 4) and decreases its boiling temperature. This is because pure C is the highest boiling point in the system, but is not chemically stable once we start the reaction. At reaction equilibrium ($D = 1$), the stable node for the system is a *maximum boiling ternary reactive azeotrope* where the following equation is satisfied (Barbosa and Doherty, 1988; Ung and Doherty, 1995):

$$\frac{x_A - y_A}{\nu_A - \nu_T x_A} = \frac{x_B - y_B}{\nu_B - \nu_T x_B}, \quad (11)$$

where $\nu_A = \nu_B = -1$, $\nu_T = -1$, and the liquid-vapor mixture is in simultaneous phase and chemical equilibrium. Equation 8 is consistent with Eq. 11 in the limit as $\zeta \rightarrow \infty$ and D approaching unity.

Branch 1 in Figure 3 originates at pure A as an unstable node (Figure 2a). At $D \approx 0.25$ there is a bifurcation and a saddle (Branch 2) that is outside the composition space for $D < 0.2$, meets Branch 1 and exchanges stability with it. That is, Branch 1 becomes a saddle for higher values of D , while Branch 2 becomes an unstable node (the origin of trajectory-

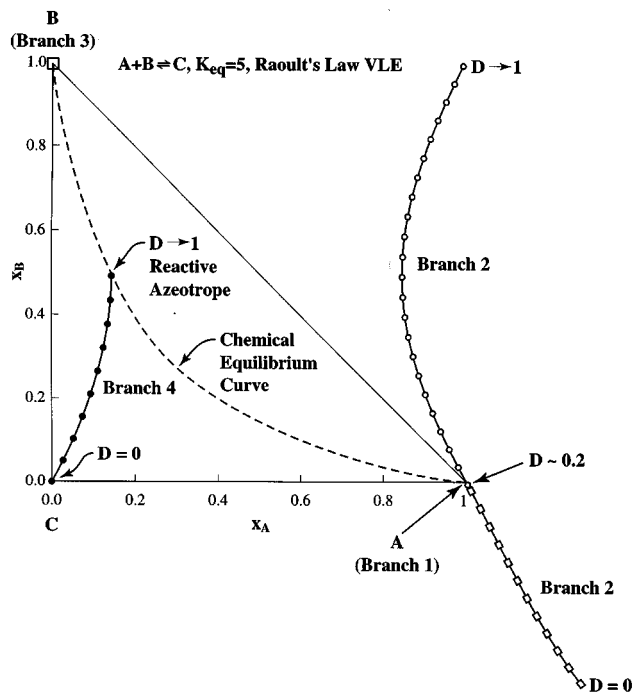


Figure 4. Solution branches on a phase plan for the hypothetical ternary mixture of A, B and C with the chemical reaction $A + B \rightleftharpoons C$, $K_{eq} = 5$ at 1 atm.

As $D \rightarrow 1$, Branch 2 approaches the point $x_A = 1$ and $x_B = 1$, as explained in the text.

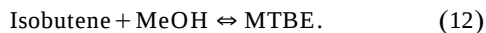
res; see Figure 2b) and remains outside the composition triangle (Figure 4). Even though Branch 2 lies outside the triangle, it has a significant influence on the trajectories inside the triangle, as illustrated in Figure 2b. In the limit $D \rightarrow 1$, this branch approaches a special fixed point ($\nu_A/\nu_T, \nu_B/\nu_T$), which is at $x_A = 1$ and $x_B = 1$ in this example. That this is a fixed point at $D \rightarrow 1$ can easily be shown from Eq. 8. In this example, this point is the source (unstable node) for the residue curves in the limit of very fast reactions. In general, the residue curves in this limit are straight lines and closely approach the stoichiometric lines for a single-phase reaction. This is because the reaction takes place on a time scale much faster than vaporization when $D \rightarrow 1$, so that the behavior in the liquid phase closely approaches that of a single-phase reactor until the combined phase and reaction equilibrium constraint is approached. Using other arguments, Hauan and Lien (1998) first showed that the stoichiometric lines all intersect at this special fixed point.

If we restrict our attention to the chemical equilibrium curve in Figure 4, as we would if the analysis were based on transformed compositions, pure A appears to be an unstable node even though it is actually a saddle in the full composition space. This is because the equilibrium curve is the unstable manifold of the saddle at A. This fact is useful for understanding the relationship between the phase planes for $D = 1$ and those at $D \rightarrow 1$. This limit is not smooth, because the dimensionality of the equilibrium reactive system is lower than that of the kinetically controlled system by the number of independent chemical reactions (Ung and Doherty, 1995).

We have found the continuation approach to be a robust method for calculating all of the surviving pure components and nonreactive azeotropes as well as the reactive azeotropes in a mixture at phase and chemical equilibrium (Huss et al., 1997).

The MTBE System

The production of high-octane-gasoline blending components has gained great economic importance recently, because of lead phasedown programs [required by the U.S. Clean Air Amendment (Rock, 1992) and also because of the reduction of aromatics and butane in gasoline. Various oxygen-containing compounds like alcohols and ethers have proven suitable for octane enhancement (see, e.g., Prezelj, 1987). The most important of these components is methyl *tert*-butyl ether (see, e.g., Oost and Hoffmann, 1996). MTBE is made by reacting isobutene and methanol in the liquid phase at temperatures in the range of 40 to 100°C using sulfuric acid (Al-Jarallah et al., 1988; Al-Jarallah, private communication, 1993) or an ion exchange resin (Rehfinger and Hoffmann, 1990) as catalyst. The principal reaction is



The VLE parameters, thermodynamic equilibrium constant, the rate equation, and reaction rate constant were taken from Venimadhavan et al. (1994, 1995). The reference temperature for defining Da was chosen to be the minimum temperature on the boiling surface at a pressure of 8 atm; this is the boiling point of the isobutene-methanol azeotrope at 60.18°C. The reference forward reaction rate constant at this temperature is $k_{f,\text{ref}} = 5.24 \times 10^{-3} \text{ min}^{-1}$.

Figure 5 shows the bifurcation diagram. The left end of the diagram represents the nonreactive system. There are five singular points, the isobutene-methanol azeotrope, which is the unstable node, pure isobutene, and the methanol-MTBE azeotrope, which are saddles, and pure methanol and MTBE, which are stable nodes. As D increases, the azeotrope between isobutene and methanol cannot be a solution to the equations, because it reacts to give a three-component mixture. The solution branch for the unstable node originating at the azeotrope for $D = 0$ moves outside of the feasible composition space, but its effect is still apparent for the feasible trajectories inside. As in the first example, we expect a solution at the point $(\nu_{\text{isobutene}}/\nu_T, \nu_{\text{MeOH}}/\nu_T)$, that is, $x_{\text{isobutene}} = 1$ and $x_{\text{MeOH}} = 1$, as $D \rightarrow 1$. However, solutions on this unstable node branch reach a point ($D = 0.872$) where roots to the vapor-liquid phase equilibrium problem become complex due to the negative mole fractions of MTBE; we have not continued calculations beyond this point.

The stable node that originated at the pure MTBE vertex moves into the composition space and merges with the saddle that started at the methanol-MTBE azeotrope at $D = 0.1424$ ($Da = 0.167$), where a turning-point bifurcation occurs. After that, the system has only one stable node (pure methanol); all residue curves end at the pure methanol vertex. When the two singular points meet and cancel each other, however, they leave behind a severe tangent pinch, which is very difficult to cross by distillation. This tangent pinch actually is advantageous in the reactive distillation of MTBE because it pro-

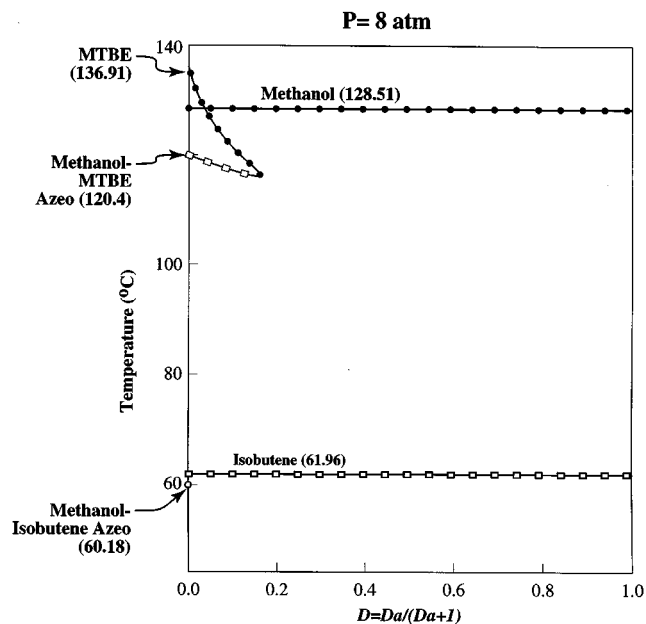


Figure 5. Bifurcation diagram for the MTBE system at 8 atm.

vides a composition rich in MTBE from the bottom of the reactive zone of a continuous distillation column. This mixture can then be separated using a nonreactive zone, thus giving pure MTBE as the bottom product from the column.

It can be helpful to plot the corresponding compositions on a phase plane, as shown in Figure 6. The nonreactive sys-

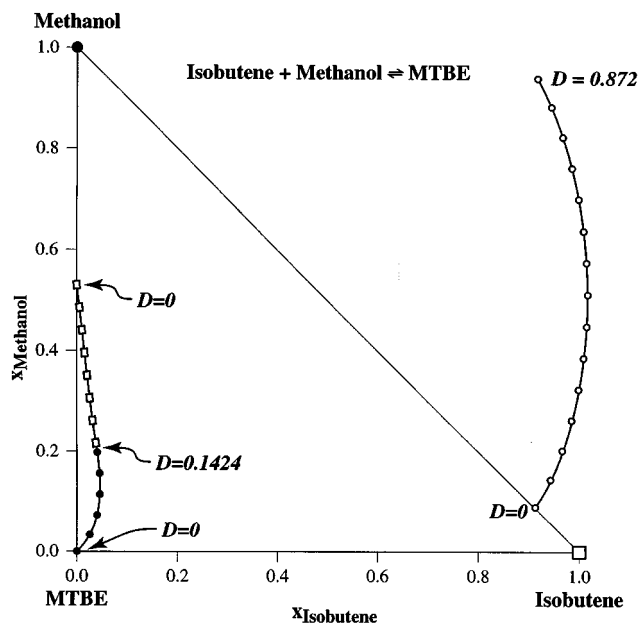


Figure 6. Solution branches on a phase plane for the MTBE system at 8 atm.

The branch beginning at the isobutene-methanol azeotrope was not calculated beyond $D = 0.872$, because the roots for the phase equilibrium problem take on complex values for higher D .

tem has two stable nodes (methanol and MTBE), two saddles (isobutene and the methanol-MTBE azeotrope), and one unstable node (the isobutene-methanol azeotrope). As soon as the reaction starts the unstable node moves outside the composition space. The stable node that was at pure MTBE and the saddle that was at the methanol-MTBE azeotrope move into the composition space and meet at a critical value of Da , where they disappear and leave a tangent pinch in their wake. For all practical purposes, the tangent pinch is like a stable node for all trajectories that originate in the isobutene-rich corner of the diagram because it would take a large number of stages to get past it. As we increase Da , this pinch moves toward the reaction equilibrium curve, which it reaches when the system is at reactive equilibrium ($D = 1$).

$$r = \frac{Wk'_{s,1} \left(a_{\text{HOAc}} a_{\text{MeOH}} - \frac{a_{\text{MeOAc}} a_{\text{H}_2\text{O}}}{K_{\text{eq}_1}} \right)}{\left(1 + K_{\text{HOAc}} a_{\text{HOAc}} + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{MeOAc}} a_{\text{MeOAc}} + K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}} \right)^2}, \quad (15)$$

Phase planes for the compositions can also be found for this example (Venimadhavan et al., 1994, 1995; Thiel et al., 1997). Venimadhavan et al. (1994, 1995) show selected RCM at various values of Da for this mixture at a pressure of 8 atm. Clearly, a bifurcation occurs between $Da = 0.12$ and $Da = 0.5$ in agreement with the bifurcation diagram in Figure 5.

The first two examples help to identify and interpret the main features of the bifurcation diagrams using the phase plane as an auxiliary tool. The next example is a five-component mixture with two reactions, and we cannot plot the phase space. Hence, we have to rely exclusively on the bifurcation diagrams.

Methyl Acetate/DME System

We consider the esterification of acetic acid with methanol to form methyl acetate and water:



This is a classic example for the application of reactive distillation, which is attractive for several reasons. The extent of reaction in a conventional liquid-phase reactor is restricted by chemical equilibrium (Agreda and Partin, 1984; Agreda et al., 1990). The conventional process is also expensive because the outlet from the reactor contains a complicated mixture of components, which requires an extraction and a complex distillation sequence to separate. This involves the addition of extraneous solvents and entrainers, which lead to increased costs for their recovery and recycle. The primary product (methyl acetate) forms a minimum boiling azeotrope with one of the reactants (methanol), however, and if this azeotrope could be continuously removed from the mixture, the conversion would increase and the rate would be enhanced. In contrast to the conventional liquid-phase process, reactive distillation offers a cleaner, cheaper alternative (Agreda et al., 1990).

For a bifurcation analysis, the equilibrium and kinetic models were taken from Song et al. (1997). The thermodynamic equilibrium constant as a function of temperature is

$$\ln(K_{\text{eq}_1}) = 0.83983 + \frac{782.98}{T}, \quad (14)$$

where T is in K. In the temperature range of interest, K_{eq} ranges from approx. 20 to 30, which is significantly higher than the value of $K_x = 5.2$ in earlier work (Agreda et al., 1990). Most of this difference is due to nonideal liquid-phase behavior; using a UNIFAC estimate for K_γ (the ratio of the activity coefficients of the products to the activity coefficients of the reactants), their corresponding value of K_{eq} is 14.7.

Experiments were performed on a heterogeneous catalyst (Amberlyst 15W, Rohm and Haas Company) and a heterogeneous Langmuir-Hinshelwood/Hougen-Watson kinetic model was used to correlate the results, that is,

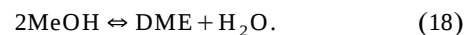
where $k'_{s,1}$ is the apparent forward rate constant given by

$$\ln(k'_{s,1}) = 24.64 - \frac{6,287.7}{T}, \quad (16)$$

where T is in K, and $k'_{s,1}$ has units of (mol of mixture) (mol of H^+ ions) $^{-1} \text{ min}^{-1}$, and the adsorption equilibrium constants are assumed to be independent of temperature:

$$K_{\text{H}_2\text{O}} = 10.50, \quad K_{\text{MeOH}} = 4.95, \quad K_{\text{HOAc}} = 3.18, \\ K_{\text{MeOAc}} = 0.82. \quad (17)$$

Since reactive distillation processes operate at the boiling temperature of a mixture, an increase in the pressure leads to an increase in the overall reaction rate and potentially a reduction in equipment size. On the other hand, an increase in boiling temperature lowers the reaction equilibrium constant for exothermic reactions leading to lower equilibrium conversions. The increase in boiling temperature can also trigger unwanted side reactions. To study the effect of pressure, we account for a side reaction, namely, the dehydration of methanol to dimethyl ether and water. The reaction is



The reaction equilibrium constant for the DME reaction was obtained from (Nisoli et al., 1997):

$$K_{\text{eq}_2} = \exp\left(-\frac{\Delta G^0}{RT}\right), \quad \Delta G^0 = -2.4634 - 1.5167 \times 10^{-3} \times T, \quad (19)$$

where ΔG^0 is the free energy of the reaction in kcal/mol and T is the temperature in K. The LHHW model for the DME reaction, assuming that DME is extremely volatile and does not have a significant presence on the catalyst surface, is

$$r = \frac{Wk'_{s,2}K_{\text{MeOH}}^2 \left(a_{\text{MeOH}}^2 - \frac{a_{\text{DME}}a_{\text{H}_2\text{O}}}{K_{\text{eq}_2}} \right)}{(1 + K_{\text{MeOH}}a_{\text{MeOH}} + K_{\text{H}_2\text{O}}a_{\text{H}_2\text{O}})^2}. \quad (20)$$

The apparent rate constant $k'_{s,2}$ can be expressed as

$$\ln(k'_{s,2}/W) = 27.40 - \frac{10,654.0}{T}, \quad (21)$$

where T is in K and $k'_{s,2}$ has the same units as $k'_{s,1}$. The adsorption equilibrium constants were assumed to have the same values as before. The VLE was modeled by the Wilson equation (for the pure component Antoine and the Wilson binary interaction parameters, see Table 2).

The reference rate constant is defined as the forward reaction rate constant of the main reaction at a reference temperature chosen as the boiling temperature of the lowest boiling component in the mixture (DME) at 1 atm, $T_{\text{ref}} = -24.72^\circ\text{C}$, and the corresponding $k'_{s,1,\text{ref}} = 0.51$. The Damköhler number is

$$Da = \frac{H_0/V_0}{1/(k'_{s,1,\text{ref}}W)}. \quad (22)$$

For a system with multiple reactions, the extension of Eq. 8 is

$$\frac{dx_i}{d\xi} = (1-D)(x_i - y_i) + D \sum_{j=1}^N (\nu_{i,j} - \nu_{T,j}x_i)\Re_j, \quad i = 1, \dots, (R+P-1) \quad (23)$$

where

$$\Re_j = \frac{r_j}{k_{f,1,\text{ref}}} \quad j = 1, \dots, N \quad (24)$$

and r_j is the rate of reaction for reaction j ; $\nu_{i,j}$ is the stoichiometric coefficient for component i in reaction j ; $\nu_{T,j}$ is the sum of the stoichiometric coefficients for reaction j ; and N is the total number of independent reactions in the system. For heterogeneous reactions above, $k_{p,1} = Wk'_{s,1}$.

Bifurcation analysis for the methyl acetate/DME system

The amount of dimethyl ether formed is not significant at a pressure of 1 atm. At this pressure the reaction mixture consists of four components, acetic acid, methanol, methyl acetate, and water. The lightest boiler is the azeotrope between methanol and methyl acetate. There are four intermediate boilers, namely, the methyl acetate-water azeotrope, methyl acetate, methanol, and water. The heaviest boiler is acetic acid. The residue curve map is shown in Figure 7. All trajectories start at the light boiler (the methanol-methyl acetate azeotrope) and end at the heavy boiler (acetic acid). The bifurcation diagram at a pressure of 1 atm is given in Figure 8. Following our convention, we have not shown any branches for which the compositions travel outside the space of positive mole fractions that sum to unity. There are six singular points in the nonreactive system ($D = 0$). As soon as the reaction starts, the singular point at the methyl acetate-water azeotrope moves into infeasible (negative) composition space. This is because the components of the azeotrope start reacting (compare with the methanol-isobutene azeotrope in the MTBE system, Figure 6).

At a critical D , the branch that started as an unstable node at the methanol-methyl acetate azeotrope undergoes a bifurcation. The unstable node moves out of the composition space. The methanol-methyl acetate azeotrope continues to be a solution, but it is now a saddle instead of an unstable node (compare this with pure component A in the hypothetical system, Figure 4). The other branches continue to be solutions with the same stabilities until the equilibrium limit. At the equilibrium limit, the lightest boiler is the methanol-methyl acetate azeotrope, which can be taken off the top of a reactive distillation column. This result is consistent with the

Table 2. Thermodynamic Data for the MeOAc/DME Example*

Component	Constants for the Antoine Equation			
	A	B	C	V_i (m ³ /mol)
Acetic Acid (1)	22.1001	-3,654.62	-45.392	57.54×10^{-6}
Methanol (2)	23.49989	-3,643.31362	-33.434	44.44×10^{-6}
Methyl Acetate (3)	21.1520	-2,662.78	-53.460	79.84×10^{-6}
Water (4)	23.2256	-3,835.18	-45.343	18.07×10^{-6}
DME (5)	21.2303	-2,164.85	-25.344	69.07×10^{-6}
Binary interaction parameters for the Wilson equation				
$A_{11} = 0.0$	$A_{21} = -547.5248$	$A_{31} = -696.5031$	$A_{41} = -658.0266$	$A_{51} = 96.7797$
$A_{12} = 2,535.2019$	$A_{22} = 0.0$	$A_{32} = -31.1932$	$A_{42} = 469.5509$	$A_{52} = -418.6490$
$A_{13} = 1,123.1444$	$A_{23} = 813.1843$	$A_{33} = 0.0$	$A_{43} = 1,918.232$	$A_{53} = -21.2317$
$A_{14} = 237.5248$	$A_{24} = 107.3832$	$A_{34} = 645.7225$	$A_{44} = 0.0$	$A_{54} = 522.2653$
$A_{15} = -96.7798$	$A_{25} = 900.9358$	$A_{35} = -17.2412$	$A_{45} = 703.3566$	$A_{55} = 0.0$

* The Antoine equation is $\ln(P^{\text{sat}}) = A + B/(T + C)$, with P^{sat} in Pa, and T in K.

The Wilson equation is $\ln(\gamma_i) = 1 - \ln\left(\sum_{j=1}^C x_j \Lambda_{i,j}\right) - \sum_{k=1}^C \left(\frac{x_k \Lambda_{k,i}}{\sum_{j=1}^C x_j \Lambda_{k,j}}\right)$, where $\Lambda_{i,j} = \frac{V_j}{V_i} \exp\left(\frac{-A_{i,j}}{RT}\right)$ with V_j in m³/mol, and $A_{i,j}$ in cal/mol

and $A_{ij} = 0$ implies ideality.

The dimerization constant for acetic acid in the vapor phase is $\log_{10}(K_D) = -12.5454 + (3,166.0/T)$ with T in K.

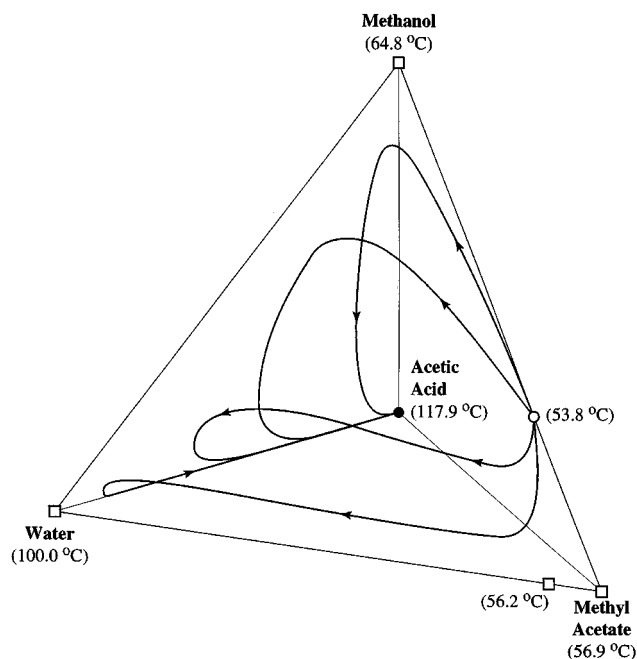


Figure 7. Residue curve map for a mixture of acetic acid, methanol, methyl acetate, and water with no chemical reactions ($Da = 0$) and at 1 atm.

RCM at chemical equilibrium, shown in Figure 9 in transformed variables. From this figure, we can also see that if an excess of methanol is fed to a continuous column, we could get the methanol-methyl acetate azeotrope off the top and

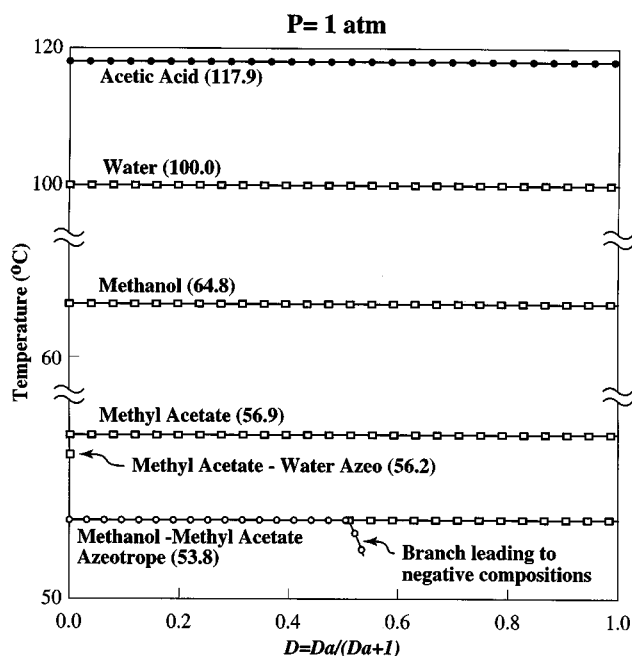


Figure 8. Bifurcation diagram for the methyl acetate system at 1 atm.

The branch leading to negative compositions was not calculated beyond the point shown because solutions to the phase equilibrium model become complex.

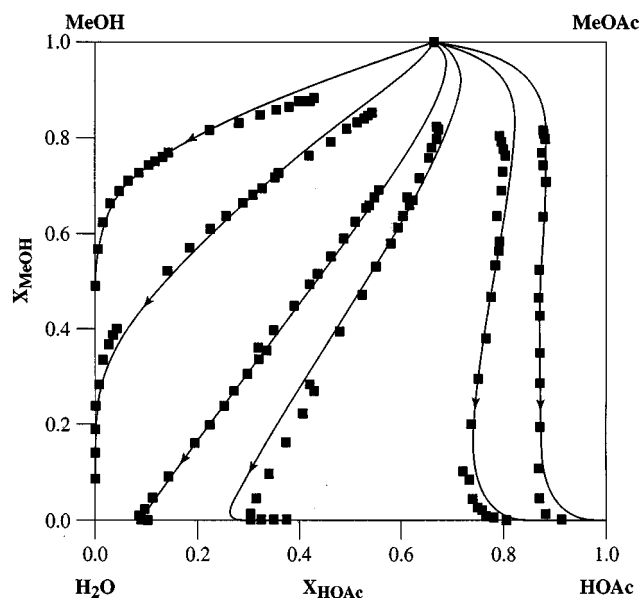


Figure 9. Computed (solid line) vs. measured (symbols) residue curves for the methyl acetate system at 1 atm.

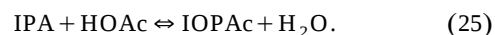
Reproduced from Song et al., 1998.

water off the bottom, keeping the acetic acid inside the column at all times.

As the pressure is increased, DME starts to form via reaction 18. In the five-component mixture, DME is the lightest boiler (unstable node) followed by the methanol-methyl acetate azeotrope, methanol, the methyl acetate-water azeotrope, methyl acetate, water, and acetic acid, which is the heaviest boiler. These seven singular points are shown at the nonreactive (left) edge of the bifurcation diagram in Figure 10 at a pressure of 10 atm. As soon as the reaction is initiated, some of the azeotropes and pure components cease to be solutions. The branches that begin at these azeotropes and pure components move out of the composition space; these are not shown on the bifurcation diagram. At the equilibrium limit, there are four singular points: DME, which is still the unstable node; methyl acetate and water, which are the intermediate boilers; and acetic acid, which is the stable node. Figure 11 gives the equilibrium RCM for this mixture in transformed variables. We see that a feed of methanol and acetic acid can give DME as an overhead product from a reactive distillation column and a mixture of water and acetic acid as a bottom product. The production of methyl acetate is not favored at the equilibrium limit at 10-atm pressure.

Isopropyl Acetate System

A final example is similar to the last, but with isopropanol instead of methanol and with no side reactions. We wish to illustrate in this example that the bifurcation analysis can give a *qualitative* idea of the behavior even when we do not have a detailed kinetic model for the reaction. This is potentially useful in planning experiments. The reaction is



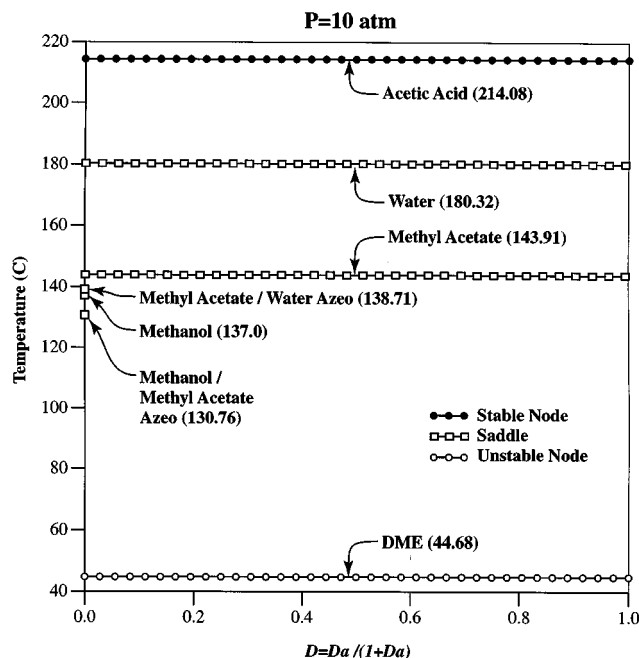


Figure 10. Bifurcation diagram for the methyl acetate/DME system at 10 atm.

In the absence of a rate expression we represent the kinetics by the pseudohomogeneous model

$$r = k_f \left(a_{\text{HOAc}} a_{\text{IPA}} - \frac{a_{\text{IPOAc}} a_{\text{H}_2\text{O}}}{K_{\text{eq}}} \right), \quad (26)$$

in which we assume k_f is independent of temperature, so that $k_f/(k_{f,\text{ref}}) = 1$. The thermodynamic equilibrium constant has a value of approximately 8.7 in the temperature range of interest (Lee and Kuo, 1996). Nonidealities in the liquid phase were modeled using the NRTL equation (for the pure component Antoine and the NRTL binary interaction parameters, see Table 3). The vapor-phase dimerization of acetic acid was taken into account in the VLE modeling. Only one parameter remains, D , which is varied from zero to unity.

Figure 12 shows the bifurcation diagram. At the nonreactive limit ($D = 0$), the minimum boiling ternary azeotrope between isopropanol, isopropyl acetate, and water is the lightest boiler (unstable node). There are six intermediate boiling species, and acetic acid is the heaviest (stable node). As soon as the reaction is initiated, the minimum boiling ternary azeotrope and the isopropyl acetate-water binary azeotrope react away. The next three branches (in order of increasing boiling points) are more interesting.

As the amount of reaction is increased, a critical value is reached ($D \approx 0.55$) where the isopropanol branch bifurcates from a saddle to a stable node. For higher values of D , there are two stable nodes in the system, isopropanol and acetic acid. This implies the existence of a distillation boundary; depending on the feed composition, we can obtain either acetic acid or isopropanol out of the bottom of a column. There is also a quaternary saddle singular point in the system for values of D between ≈ 0.55 and ≈ 0.71 . Further, at $D \approx 0.82$,

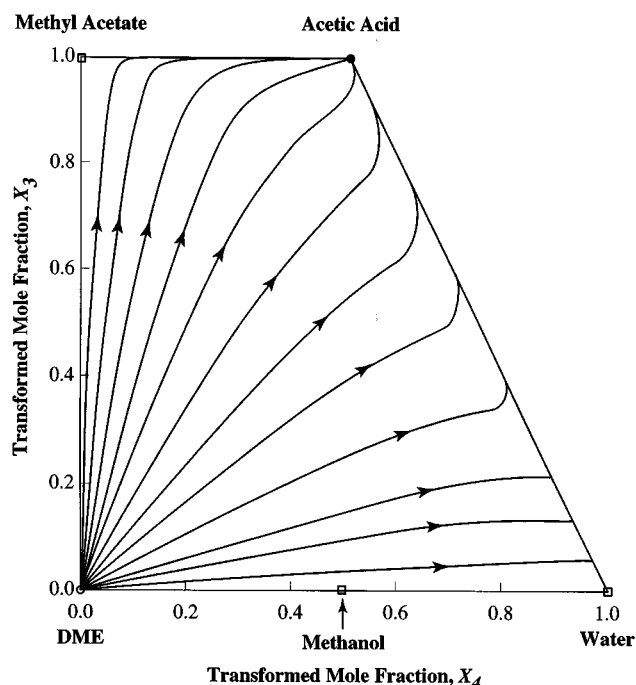


Figure 11. Equilibrium residue curve maps for the methyl acetate/DME system at 1 atm.

The transformed mole fractions are those defined by Ung and Doherty (1995); HOAc and MeOH are the reference components, giving $X_3 = x_{\text{MeOAc}} + x_{\text{HOAc}}$ and $X_4 = x_{\text{H}_2\text{O}} + \frac{1}{2}x_{\text{HOAc}} + \frac{1}{2}x_{\text{MeOH}}$.

Table 3. Thermodynamic Data for the iso-Propyl Acetate Example*

Component	Constants for the Antoine Equation		
	A	B	C
Acetic acid (1)	23.3618	-4457.83	-14.699
Isopropanol (2)	25.3358	-4628.96	-20.514
Isopropyl Acetate (3)	21.7798	-3307.73	-39.485
Water (4)	23.4776	-3984.92	-39.724
Binary interaction parameters for the NRTL equation			
$a_{11} = 0.0$	$a_{21} = 81.3926$	$a_{31} = 154.7885$	$a_{41} = 842.6081$
$a_{12} = -281.4482$	$a_{22} = 0.0$	$a_{32} = 140.0972$	$a_{42} = 1,655.2550$
$a_{13} = 141.0082$	$a_{23} = 269.9609$	$a_{33} = 0.0$	$a_{43} = 1,270.2036$
$a_{14} = -219.7238$	$a_{24} = 39.8541$	$a_{34} = 1,165.709$	$a_{44} = 0.0$
$\alpha_{11} = 0.0$	$\alpha_{21} = 0.3048$	$\alpha_{31} = 0.3014$	$\alpha_{41} = 0.2997$
$\alpha_{12} = 0.3048$	$\alpha_{22} = 0.0$	$\alpha_{32} = 0.3009$	$\alpha_{42} = 0.3255$
$\alpha_{13} = 0.3014$	$\alpha_{23} = 0.3009$	$\alpha_{33} = 0.0$	$\alpha_{43} = 0.3300$
$\alpha_{14} = 0.2997$	$\alpha_{24} = 0.3255$	$\alpha_{34} = 0.3300$	$\alpha_{44} = 0.0$

*The Antoine equation is $\ln(P^{\text{sat}}) = A + B/(T + C)$, with P^{sat} in Pa, and T in K.

The NRTL equation is

$$\ln(\gamma_i) = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right),$$

where $G_{ij} = e^{[-\tau_{ij}\alpha_{ij}]}$ $\tau_{ij} = (a_{ij} + b_{ij}T)/RT$.

Note: All the $b_{ij} = 0$ here and $\alpha_{ij} = \alpha_{ji}$.

The dimerization constant for acetic acid in the vapor phase is $\log_{10}(K_D) = -12.5454 + (3,166.0/T)$ with T in K.

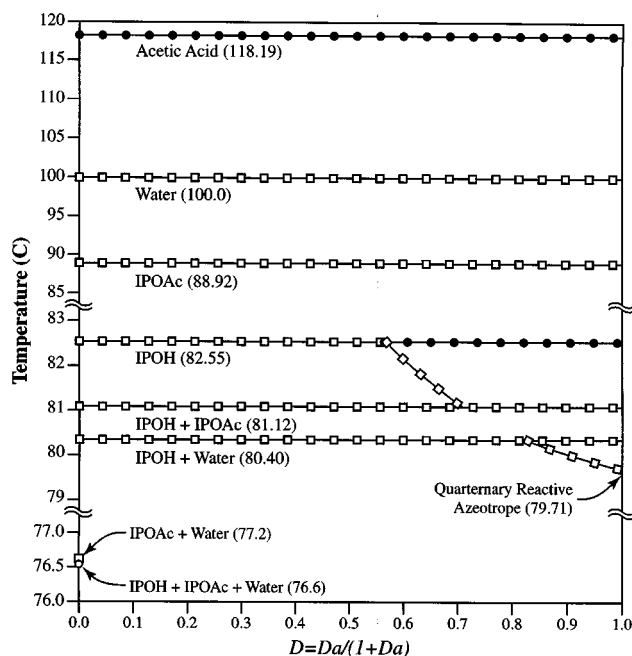


Figure 12. Bifurcation diagram for the isopropyl acetate system at 1 atm.

there is a bifurcation on the binary isopropanol-water azeotrope branch. This bifurcation is very interesting because it leads to a quaternary *reactive* azeotrope at equilibrium. Therefore, our modeling and analysis predict the existence of a minimum-boiling reactive azeotrope in this mixture. Experiments have recently proved the existence of this reactive azeotrope (Song et al., 1997).

This example demonstrates that the bifurcation analysis can give a good qualitative estimate for the behavior of a reactive system, even when we do not have any information about the reaction kinetics. The positions where the bifurcation points occur will depend on the details of the kinetic model. Because the bifurcation analysis scans the whole reaction space ($0 \leq D \leq 1$), we believe that this approach will give good first estimates of the main features of the system behavior *before* the rate model is developed.

Conclusions

A model has been developed to describe a simple distillation process with multiple chemical reactions of arbitrary stoichiometry. A bifurcation analysis of this model provides a systematic way of studying the effects of kinetics on the RCM and thus on the feasibility of separations for reactive distillation as shown for four example systems.

For low and high Damköhler number, the lightest and heaviest boiling components or azeotropes are known or can be found by known methods. In those limits, the products from a distillation can be anticipated, that is, unstable nodes are potential distillate products and stable nodes are potential bottom products. The presence of distillation boundaries can also be detected, for example, by the presence of more than one stable node or more than one unstable node. The corresponding feasible separation structures can also be

identified, and these depend on the feed composition when there are distillation boundaries. The feasible structures in the limiting cases of low and high Da are not the same and there are one or more transitions. *Thus, different structures are feasible for different ranges of the Damköhler number. Conversely, any given structure may or may not be feasible as the reaction rate or residence time is changed, so that the feasibility of a given separation may depend on production rates.* The transition points correspond to bifurcations and the approach described here is a systematic method for calculating and representing these changes using bifurcation analysis and continuation methods.

The isopropyl acetate example illustrates the appearance of a fixed point leading to a reactive azeotrope, so that too much catalyst or residence time, that is, too large a Damköhler number, can be detrimental to achieving high purities. This example also shows that the bifurcation study can capture the essential features of a kinetically controlled reactive distillation system even if we do not have a good rate model. This would be useful in cases where we have little kinetic information.

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Notation

- a_i = activity of component i
- A_i = generic chemical species
- K_i = adsorption equilibrium constant for component i
- P = total number of products
- $\mathcal{R}$ = normalized reaction rate, dimensionless
- R = total number of reactants
- W = normalized catalyst concentration, mol H^+ ions/mol of mixture
- X_i = transformed liquid-phase mole fraction

Subscripts

- p = products
- r = reactants
- 0 = initial value

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