# Synthesis of ETBE: Residue curve maps for the heterogeneously catalysed reactive distillation process

## Christian Thiel, Kai Sundmacher, Ulrich Hoffmann *

*Institut für Chemische Verfahrenstechnik, Technische Universität Clausthal Leibnizstraße 17, D-38678 Clausthal-Zellerfeld, Germany*

## Abstract

The liquid phase synthesis of octane-enhancing ethers is increasingly realized as a reactive distillation process, catalysed by ion exchange resins. To study the physical and chemical phenomena occurring in these systems, the present paper considers a reactive batch distillation process in a heated still. Because of its increasing technical importance, the synthesis of ETBE (ethyl tertiary butyl ether) from ethanol and isobutene is investigated as an example.

The developed model is based on the phase equilibrium between the liquid and vapour phases and an adequate kinetic formulation of the heterogeneously catalysed etherification by application of generalized Langmuir–Hinshelwood rate expressions. To describe the non-ideal mixture behaviour, the liquid phase activities are introduced. Simulation results show that the shape of the residue curves depends on two essential parameters: the Damköhler number, Da, and the operating pressure, $p$. The values of these parameters influence the existence and the position of fixed points in the residue curve map. Therefore an analysis is carried out to calculate the steady state solutions in the reactive mixture and to forecast the number of stable nodes with given Da and $p$. © 1997 Elsevier Science S.A.

*Keywords:* Residue curve maps; Simple reactive distillation process; Heterogeneously catalyzed etherification; Synthesis of fuel ether ETBE; Study of parameters; Analysis of steady state solutions

## 1. Nomenclature

| | |
|---|---|
| $A$ | constant, Table 1 |
| $a_i$ | liquid phase activity of component $i$ |
| $B$ | constant, Table 1 |
| $C$ | constant, Table 1 |
| $c_L$ | mean acid group concentration on the catalyst/ eq m$^{-3}$ |
| $D$ | constant, Table 1 |
| Da | Damköhler number |
| | $\equiv \dfrac{c_L \cdot k_f(T^*) \cdot V^o_{cat}}{\dot{V}^o}$ |
| $E_A$ | activation energy/kJ mol$^{-1}$ |
| $H$ | molar liquid holdup/mol |
| $\Delta_R H^0_{298}$ | standard enthalpy change of reaction at $T = 298$ K |
| $K_a$ | chemical equilibrium constant based on activities |
| $k_f$ | rate constant of reaction $j$/mol (s eq)$^{-1}$ |

| | |
|---|---|
| $M$ | number of reactions |
| $N$ | number of components |
| $p$ | pressure/MPa |
| $p_i^s$ | vapour pressure of component $i$/MPa |
| $Q$ | heating input/W |
| $R$ | universal gas constant = 8.31441 J (K mol)$^{-1}$ |
| $r_j$ | intrinsic rate of reaction $j$/mol (s eq)$^{-1}$ |
| $T$ | temperature/K |
| $T^*$ | reference temperature = 333 K |
| $V_{cat}$ | wetted volume of catalyst/m$^3$ |
| $\dot{V}$ | vapour molar flow rate/mol s$^{-1}$ |
| $X_i$ | transformed liquid mole fraction of component $i$, defined in Eq. (25) |
| $x_i$ | liquid phase mole fraction of component $i$ |
| $Y_i$ | transformed vapour mole fraction of component $i$, defined in Eq. (26) |
| $y_i$ | vapour phase mole fraction of component $i$ |

*Greek letters*

| | |
|---|---|
| $\gamma_i$ | liquid activity coefficient |
| $\nu_j$ | sum of stoichiometric coefficients in reaction $j$ |

* Corresponding author. Fax: +49 5323 72 2182; e-mail: icvt@itv.tu-clausthal.de

| $\nu_{i,j}$ | stoichiometric coefficient of component $i$ in reaction $j$ |
| $\tau$ | dimensionless time |

*Superscripts*

| ° | initial condition |

*Subscripts*

| crit | critical |
| $i$ | component index |
| $j$ | reaction index |
| + | forward reaction |
| − | reverse reaction |

*Abbreviations*

| CE | chemical equilibrium |
| DB | distillation boundary |
| ETBE | ethyl tertiary butyl ether |
| EtOH | ethanol |
| IB | isobutene |
| MeOH | methanol |
| REA | reaction vector |
| SEP | separation vector |
| $SEP_{REA}$ | part of SEP with the direction of REA |

## 2. Introduction

The combined simultaneous performance of a chemical reaction and a multicomponent distillation process is an alternative that is increasingly installed for the production of large-scale relevant chemicals. The use of this so-called reactive distillation process (RDP) can offer several advantages:

• reduced downstream processing,
• utilization of heat of reaction for evaporation of liquid phase,
• simple temperature control of the reactor,
• possibility of influencing chemical equilibrium by removal of products, and
• overcoming of limitations imposed by azeotropic mixtures.

The application of this technology is quite attractive for the heterogeneously catalysed production of fuel ethers such as MTBE (methyl tertiary butyl ether), TAME (tertiary amyl methyl ether) or ETBE, but also for homogeneously catalysed esterifications or hydrations because their formation is effected by chemical equilibrium. This technology is often referred to as catalytic distillation and can be carried out in stage towers or in packed columns where the catalyst has the shape of a packing element.

However, reactive distillation is not advantageous in every case; therefore there is a need for systematic investigations concerning the phenomena which are generated by the combination of a chemical reaction with distillation.

A common way to represent nonreactive distillation behaviour is by graphical illustration in residue curve maps (RCM). In these figures the change in time of the liquid phase composition is plotted, calculated for a simple distillation process. In our recent work [1], we transferred this concept to reactive distillation by overlaying the heterogeneously catalysed synthesis of MTBE or TAME respectively. In addition to results that are in agreement with other authors [2–5], we could show that, under certain conditions, a totally new topology of the maps can appear, namely the existence of a further saddle point.

In the present paper this concept is applied to a reactive batch distillation process for the heterogeneously catalysed synthesis of ETBE from ethanol (EtOH) and isobutene (IB). To do this, a model is made available which is based on the formulation of the vapour–liquid phase equilibrium and the liquid phase kinetics of the heterogeneously catalysed chemical reaction for this reactive mixture. It is assumed for the heating policy of the system that the model differential equations are autonomous.

The simulation of the process is performed for different values of the characteristic parameters, i.e. the Damköhler number Da and the operating pressure $p$. A starting composition is given, and the residue curve maps are calculated by integrating until they reach steady state.

These maps are discussed with respect to the appealed new characteristics. In addition, the conditions for the appearance of fixed points (both stable nodes as well as saddles) in the reactive mixture ETBE/EtOH/IB are investigated.

## 3. Formulation of the model

A principle sketch of the discussed simple reactive batch distillation process is drawn in Fig. 1. A heated still is filled with the molar liquid holdup $H$, which consists of $N$ components and has the composition $\underline{x} = (x_1, \cdots, x_N)^T$. In the liquid phase, where the heterogeneous ion exchange catalyst is present, the reversible etherification

$$\text{alcohol} + iso-\text{alkene} \underset{r_-}{\overset{r_+}{\rightleftarrows}} tert-\text{ether} \tag{1}$$
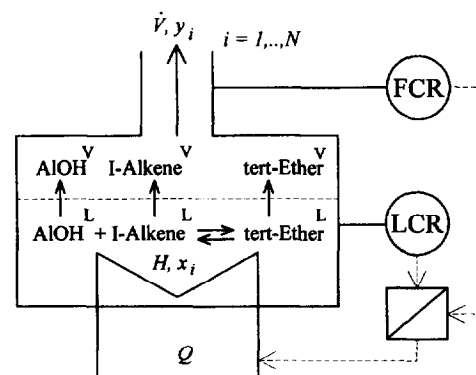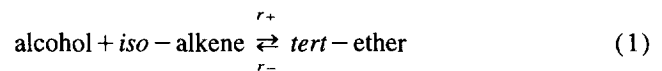


Fig. 1. Sketch of a simple reactive batch distillation process.

takes place, labelled by horizontal arrows in Fig. 1. It is also possible that several side reactions occur, e.g. isomerization of iso-alkenes, so in the following the model will be formulated with $M$ reactions. As a result of the heating input $Q$, a distillation is simultaneously carried out which leads to a mass transfer from the liquid phase into the vapour phase, labelled by vertical arrows in Fig. 1, and consequently to a vapour molar flow rate $\dot{V}$ with the composition $\underline{y} = (y_1, \cdots, y_N)^T$. The holdup $H$ and the vapour flow rate $\dot{V}$ are measured and the quotient $H/\dot{V}$ is controlled via the heating input $Q$. In the still, there is an excess of catalytically active pellets; therefore the relation between wetted catalyst volume $V_{cat}$ and holdup $H$ is assumed to be constant.

The liquid phase is in the boiling state, so that the temperature in the still corresponds to the boiling temperature $T^b$ of the liquid composition $\underline{x}$ at the given operating pressure $p$

$$T^b = T^b(\underline{x}, p) \tag{2}$$

According to this, vapour composition $\underline{y}$ and liquid composition $\underline{x}$ remain in phase equilibrium.

A combination of the material balances leads to the following equations, Eqs. (2)–(5), which describes the change with time of the mole fraction $x_i$ in the liquid phase of the still

$$\frac{dx_i}{dt} = \frac{\dot{V}}{H}(x_i - y_i) + \sum_{j=1}^{M}\left[ (\nu_{ij} - x_i \cdot \nu_j) \cdot c_L \cdot \frac{V_{cat}^o}{H^o} \cdot r_j \right]$$

$$\text{with } \nu_j = \sum_{i=1}^{N} \nu_{i,j} \quad \begin{matrix} i = 1, \ldots, N-1 \\ j = 1, \ldots, M \end{matrix} \tag{3}$$

The first term on the right hand side of Eq. (3) shows that a relation between holdup $H$ and vapour flow rate $\dot{V}$ has to be found. This quotient depends on the control system of the process. In this paper, the following heating strategy will be used

$$\frac{H}{\dot{V}} = \frac{H^o}{\dot{V}^o} = \text{const.} \tag{4}$$

This policy is physically significant and leads to an autonomous model [4]. The intrinsic reaction rate $r_j$ related to the number of acid groups of catalyst appearing in the second term on the right hand side of Eq. (3) has to be multiplied by the mean acid group concentration on the catalyst $c_L$ and the quotient of wetted volume of catalyst $V_{cat}^o$ to holdup $H^o$.

In the following, two parameters are introduced to formulate Eq. (3) in a comprehensive way. These are the dimensionless time $\tau$ and the Damköhler number Da

$$d\tau \equiv \frac{\dot{V}^o}{H^o}dt; \quad \text{Da} \equiv \frac{c_L \cdot k_f(T^*) \cdot V_{cat}^o}{\dot{V}^o} \tag{5a,b}$$

It is obvious, that the transformation defined in Eq. (5) only makes sense if the heating strategy given in Eq. (4) is valid. In Eq. (5) the rate constant of reaction $k_f$ is related to the reference temperature $T^* = 333$ K.

Consequently Eq. (3) can be written in dimensionless form as follows

$$\frac{dx_i}{d\tau} = (x_i - y_i) + \frac{\text{Da}}{k_f(T^*)}\sum_{j=1}^{M}[ (\nu_{ij} - x_i \cdot \nu_j) \cdot r_j] \quad \begin{matrix} i = 1, \ldots, N-1 \\ j = 1, \ldots, M \end{matrix} \tag{6}$$

As phase equilibrium is assumed, $y_i$ can be evaluated from the relation at boiling point

$$y_i = \frac{\gamma_i(\underline{x}, T^b) \cdot p_i^s(T^b)}{p} \cdot x_i; \quad i = 1, \ldots, N \tag{7}$$

Consequently, the appropriate equation to compute the boiling temperature $T^b$, in accordance with a combination of Eq. (7) and a summation equation in the gas phase, is

$$0 = 1 - \sum_{i=1}^{N} \frac{\gamma_i(\underline{x}, T^b) \cdot p_i^s(T^b)}{p} \cdot x_i \tag{8}$$

Since Eq. (8) cannot be explicitly solved for $T^b$, one has to use an appropriate iteration method. Hence, the turnover number $r_j$ of reaction $j$ is described by the following expression

$$r_j = r_j(\underline{x}, T^b); \, j = 1, \ldots, M \tag{9}$$

Taking into account the dependence of $T^b$ on the composition vector $\underline{x}$ and operating pressure $p$, implicitly formulated in Eq. (8), Eq. (6) can be written as

$$\frac{dx_i}{d\tau} = [x_i - y_i(\underline{x}, p)] + \frac{\text{Da}}{k_f(T^*)}$$

$$\times \sum_{j=1}^{M} [(\nu_{i,j} - x_i \cdot \nu_j)r_j(\underline{x}, p)] \quad \begin{matrix} i = 1, \ldots, N-1 \\ j = 1, \ldots, M \end{matrix} \tag{10}$$

To calculate the liquid mole fraction of the $N$th component $x_N$, the condition of summation in the liquid phase is used

$$1 = \sum_{i=1}^{N} x_i \tag{11}$$

The first term on the right hand side of Eq. (10) describes the mass transfer across the vapour–liquid interphase, i.e. the influence of distillation. In the composition space, this term can be represented by the part of the separation vector $SEP_i$, which is contributed by component $i$ [6]

$$SEP_i(\underline{x}, p) \equiv x_i - y_i(\underline{x}, p) \quad i = 1, \ldots, N-1$$

$$SEP_N(\underline{x}, p) = - \sum_{i=1}^{N-1} SEP_i(\underline{x}, p) \tag{12}$$

As shown above, $SEP_i$ depends on the liquid phase composition $\underline{x}$ and the operating pressure $p$. If $\underline{SEP} = (SEP_1 \cdots SEP_N)^T$ equals the zero-vector, no distillation occurs.

The second term on the right hand side of Eq. (10) characterizes the mass conversion in the liquid phase due to the chemical reaction. According to Hauan and Lien [6], this term denotes the part of the reaction vector $REA_i$ which is contributed by component $i$

$REA_i(\underline{x},p,\text{Da})$

$$\equiv \frac{\text{Da}}{k_f(T^*)}\sum_{j=1}^{M}[(\nu_{i,j}-x_i\cdot\nu_j)r_j(\underline{x},p)] \quad \begin{array}{l} i=1,...,N-1 \\ j=1,...,M \end{array} \quad (13)$$

$$REA_N(\underline{x},p,\text{Da}) = -\sum_{i=1}^{N-1}REA_i(\underline{x},p,\text{Da})$$

$REA_i$ shows a dependence on the liquid phase composition $\underline{x}$ and the operating pressure $p$, and additionally a dependence on the Damköhler number Da. If $\underline{REA}=(REA_1,\cdots,REA_N)^T$ equals the zero-vector, either chemical reaction is absent or the reaction is in chemical equilibrium.

So Eqs. (10)–(13) can be written vectorially as follows

$$\left(\frac{dx_1}{d\tau},\cdots,\frac{dx_N}{d\tau}\right)^T = \underline{SEP} + \underline{REA} \quad (14)$$

From Eq. (14) it is easy to derive the conditions for the existence of a steady state. The appropriate composition $\underline{x}$ is called the fixed point (FP). Hence steady state demands

$$\underline{SEP}^{FP} = -\underline{REA}^{FP} \quad (15)$$

For the sake of simplicity, in the following we will use these two vectors without underlining.

Finally it should be remembered that there are two independent parameters which determine $SEP$ and $REA$. They are:
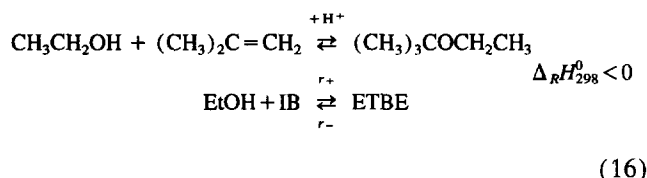
● Damköhler number Da, and
● operating pressure $p$.

## 4. Heterogeneously catalysed synthesis of ETBE

The oxygenated organic compound ethyl tertiary butyl ether (ETBE) is an excellent octane enhancer. The use of so-called fuel ethers like methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) or ETBE allows the removal of lead additives, raises combustion temperatures and improves engine efficiencies. The results are lower levels of carbon monoxide and unburned hydrocarbons in auto exhaust [7]. Among these fuel oxygenates, ETBE has some better properties than MTBE which plays the major role in the present fuel oxygenate market. The most important attrib-

utes are a higher octane rating, a higher boiling point and a lower Reid vapour pressure. In addition, the ETBE process offers an outlet for bioethanol and is currently under discussion in the United States with regard to the use of renewable raw materials [8].

On a technical scale, ETBE is produced by the liquid phase synthesis of isobutene (IB) and ethanol (EtOH). The reaction is moderately exothermic and has to be catalysed by a strong proton donor to reach an adequate rate. So the basic reaction equation can be expressed by

$$CH_3CH_2OH + (CH_3)_2C=CH_2 \underset{}{\overset{+H^+}{\rightleftarrows}} (CH_3)_3COCH_2CH_3$$

$$\Delta_R H_{298}^0 < 0$$

$$EtOH + IB \underset{r_-}{\overset{r_+}{\rightleftarrows}} ETBE$$

$$(16)$$

Potential side reactions are the dimerization and isomerization of IB, but these reactions only take place in the absence of EtOH and shall consequently be ignored in this paper.

The catalysis of the ETBE synthesis can either be done by using a homogeneous catalyst, e.g. sulphuric acid, or a heterogeneous catalyst, e.g. a strong acidic macroporous ion exchange resin. The advantages of the heterogeneously catalysed synthesis in relation to the homogeneously catalysed one are above all the simple separation of catalyst and reaction product and the minimization of waste water pollution. So in the following we will concentrate on the heterogeneously catalysed liquid phase synthesis of ETBE.

To calculate residue curve maps one has to find adequate descriptions for the thermodynamic equilibrium between the liquid and vapour phases and for the kinetics of the chemical reaction, including an expression for the chemical equilibrium.

### 4.1. VLE and chemical reaction data

Thermodynamic equilibrium between liquid and vapour phase is assumed. Consequently the following relationship between vapour and liquid phase compositions must be valid

$$y_i = \frac{\gamma_i(x,T)\cdot p_i^s(T)}{p}\cdot x_i; \quad i=1,...,N; \quad (17)$$

Table 1
Calculation methods and property data of vapour pressures for ETBE reaction systems

1. Method: Wagner equation: $\ln(p_i^s(T)/p_{crit}) = \dfrac{A\cdot(1-T/T_{crit})+B\cdot(1-T/T_{crit})^{1.5}+C\cdot(1-T/T_{crit})^3+D\cdot(1-T/T_{crit})^6}{T/T_{crit}}$

2. Method: Antoine equation: $\ln(p_i^s(T)/\text{MPa}) = A-\dfrac{B}{T/\text{K}+C}$

| Component | Reference | No. of method | Constants | | | | $T_{crit}$ | $p_{crit}$ |
|-----------|-----------|---------------|-----------|-----------|-----------|-----------|------------|------------|
| | | | A | B | C | D | | |
| Isobutene | [9] | 1 | −6.95542 | 1.35673 | −2.45222 | −1.46110 | 417.9 | 4.00 |
| Ethanol | [9] | 1 | −8.51838 | 0.34163 | −5.73683 | 8.32581 | 513.9 | 6.14 |
| ETBE | [10,11] | 2 | 7.07751 | 2778.93 | −49.1901 | − | 514.1 | 3.04 |

The vapour pressures $p_i^s$, which appear on the right hand side of Eq. (17), can be calculated using the methods and property data that are listed in Table 1.

The liquid activity coefficients $\gamma_i$ for the reactive mixture of ETBE synthesis can be computed by using the modified UNIFAC method [12,13]. The equations and parameters to evaluate $\gamma_i$ for ETBE synthesis with the aid of this model can be taken from the cited literature.

To describe the kinetics of a heterogeneously catalysed chemical reaction by a relatively simple model, one has to introduce several assumptions [14,15]:

● First of all, one has to postulate that mass transport effects inside the catalyst particle play no role in relation to the kinetics of the chemical reaction. In other words, the mass transfer resistance of the chemical reaction will be very much bigger than that caused by mass transport.

● Langmuir sorption isotherms can be assumed to describe the sorption behaviour of the components of the reaction mixture in the catalytically active gel phase of the resin.

● The sorption of EtOH in the catalytic gel phase is much stronger than those of the other components. Therefore, almost only EtOH is present at the active sites.

● The liquid phase is strongly nonideal which has to be taken into consideration by using activities $a_i = \gamma_i \cdot x_i$ instead of mole fractions $x_i$, when formulating the sorption equilibria.

Sundmacher et al. [8] propose the following rate expression (turn over number), which was developed according to the above-mentioned postulations

$$r = k_f(T) \cdot \left( \frac{a_{IB}}{a_{EtOH}} - \frac{1}{K_a} \cdot \frac{a_{ETBE}}{a_{EtOH}^2} \right) \qquad (18)$$

with $K_a$ as the chemical equilibrium constant based on liquid phase activities $a_i$. The Arrhenius equation was adapted to describe the temperature dependence of the reaction rate constant [7,8]

$$\frac{k_f(T)}{\text{mmol/(eq·s)}} = 22.3 \cdot \exp\left[ -9.694 \cdot 10^3 \left( \frac{K}{T} - \frac{1}{333.15} \right) \right] \qquad (19)$$

Finally, one has to find an expression to formulate the temperature dependence of the chemical equilibrium constant $K_a$ in the liquid phase. Vila et al. [16] give the following equation, assuming that the molar heat capacities of the species are given by polynomials of the 3rd degree

$$\ln(K_a) = 1140.912 - 14580 \cdot (T/K)^{-1} - 232.9$$

$$\cdot \ln(T/K) + 1.087 \cdot (T/K) - 1.114 \cdot 10^{-3} \qquad (20)$$

$$\cdot (T/K)^2 + 5.538 \cdot 10^{-7} \cdot (T/K)^3$$

### 4.2. Calculation of residue curve maps and results

Thus all parameters have been evaluated and the model for calculating residue curve maps of a reactive mixture of isobutene, ethanol and ETBE can be formulated

$$\frac{dx_{EtOH}}{d\tau} = f_1 = (x_{EtOH} - y_{EtOH}) + \frac{Da}{k_f(T^*)} \cdot (x_{EtOH} - 1) \cdot r \qquad (21a)$$

$$\frac{dx_{IB}}{d\tau} = f_2 = (x_{IB} - y_{IB}) + \frac{Da}{k_f(T^*)} \cdot (x_{IB} - 1) \cdot r \qquad (21b)$$

$$0 = f_3 = 1 - x_{IB} - x_{EtOH} - x_{ETBE} \qquad (21c)$$

$$0 = f_4 = 1 - \sum_{i=1}^{N} \frac{\gamma_i(x,T) \cdot p_i^s(T)}{p} \cdot x_i \qquad (21d)$$

This system of equations is composed of two ordinary differential equations: the material balances Eqs. (21a) and (21b) of ethanol and isobutene in the liquid phase, corresponding to Eq. (10). The other two algebraic equations are the condition of summation in the liquid phase (Eq. (21c)) and the condition of summation in the vapour phase (Eq. (21d)), derived from Eq. (11) and Eq. (8). This set of differential-algebraic equations (DAE) has to be solved for the liquid mole fractions $x_{EtOH}$, $x_{IB}$ and $x_{ETBE}$, and the temperature $T$. To find a numerical solution, the extrapolation solver LIMEX [17] was used, which is designed for the solution of DAE's of indices up to one. The system of Eqs. (21), is an index-one system.

For calculation, the operating pressure $p$, the Damköhler number Da, and the starting liquid composition $x$ in the still must be specified according to the algebraic Eq. (21c). For these initial conditions, the boiling temperature $T$ is calculated using the condition of summation for the vapour phase, Eqs. (21) so that the algebraic part of the DAE is fulfilled. So the appropriate initial conditions are

$$x_{EtOH}(\tau = 0) = x_{EtOH}^o;$$

$$x_{IB}(\tau = 0) = x_{IB}^o;$$

$$0 = 1 - x_{EtOH}^o - x_{IB}^o - x_{ETBE}^o;$$

$$0 = 1 - \sum_{i=1}^{N} \frac{\gamma_i(x^o, T^o) \cdot p_i^s(T^o)}{p} \cdot x_i^o \qquad (22a, b, c, d)$$

Fig. 2 shows the results of these calculations for nonreactive distillation (Da = 0). In addition, the operating pressure $p$ is varied between 0.6 and 1.0 MPa. It can be noticed that there are several fixed points with different behaviours in the maps. These include one saddle point, which is identical with the binary azeotropic point between EtOH and ETBE. The other nonreactive binary azeotropic point between EtOH and IB represents an unstable node according to the terminology of nonlinear dynamics. These two points are linked by a separatrix, which is called the distillation boundary in separation technology. Consequently two stable nodes exist in the system: one stable node at pure ETBE for initial compositions below the distillation boundary, and another stable node at pure EtOH for mixtures having an initial compound above the distillation boundary.

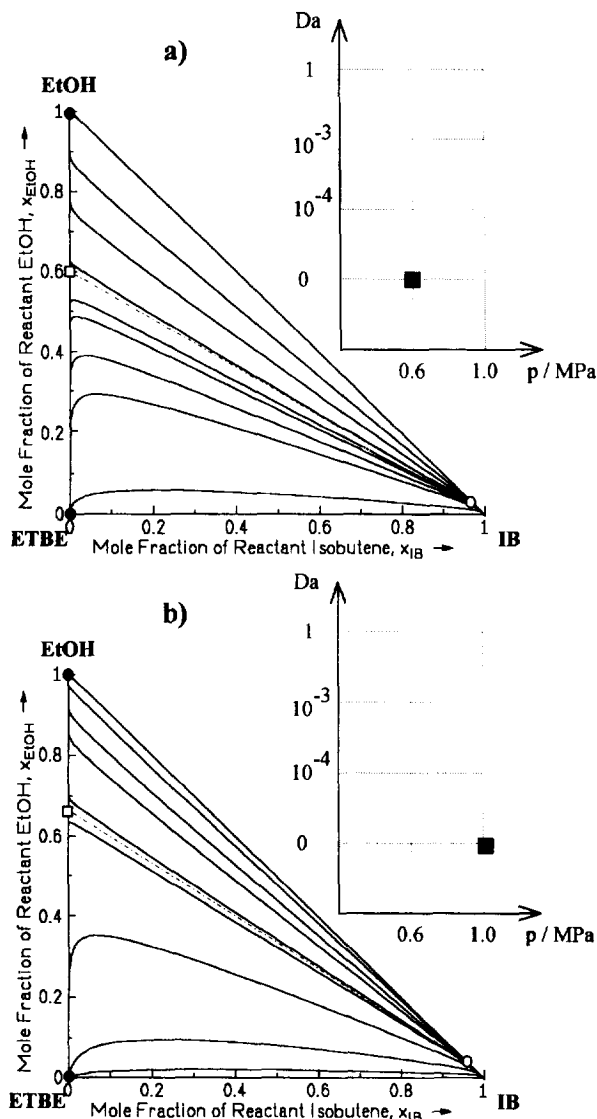The influence of operating pressure $p$ on the topology of nonreactive residue curve maps can be studied by a compar-

Fig. 2. Residue curve maps for distillation without reaction (Da = 0) at operating pressure: (a) $p = 0.6$ and (b) 1.0 MPa.

ison between Fig. 2(a) and (b). While the unstable node between EtOH and IB is only slightly influenced by the variation of pressure, $p$ has a great effect on the position of the saddle point EtOH and ETBE. With increasing $p$ this binary azeotropic point moves towards the EtOH vertex, and correspondingly the location of the separatrix is shifted.

The situation changes remarkably when chemical reaction takes place in the still. Fig. 3 shows trajectories of reactive distillation processes for ETBE synthesis. In these simulations, the Damköhler number Da is discussed as the second parameter in addition to the operating pressure $p$. Da is enhanced starting with a value of $10^{-4}$ (Fig. 3(a) and (b)) via Da $= 10^{-3}$ (Fig. 3(c) and (d)), up to Da $= 1$ (Fig. 3(e) and (f)). The operating pressure $p$ varies between 0.6 and 1.0 MPa according to Fig. 2. Increase of the Damköhler number means physically that the influence of the chemical reaction is intensified. For Da $= 10^{-4}$, the shapes of trajectories starting above the separatrix are still similar to those of distillation without reaction, so that the EtOH vertex remains a

stable node in the system. Below the separatrix, the conditions change considerably. The chemical reaction vector REA has the direction of stochiometric lines towards the chemical equilibrium [6]. Its length is directly proportional to the distance from chemical equilibrium and to Da. Consequently the stable node moves from pure ETBE to a point, which has the approximate composition 0.9ETBE, 0.08EtOH and 0.02IB ($p = 0.6$ MPa), respectively 0.8ETBE, 0.16EtOH and 0.04IB ($p = 1.0$ MPa). But the saddle, which determines the position of the separatrix, also shows a movement. In the case of distillation without reaction (Da $= 0$), the saddle coincides with the binary azeotropic point between EtOH and ETBE, but with increasing Damköhler number this point is shifted towards the ETBE vertex. The unstable node has moved out of the physically relevant composition space.

The trajectories of the fixed points, i.e. the saddles and stable nodes, will be discussed in the next section. Further enhancement of the Damköhler number to Da $= 10^{-3}$ leads to the situation that at the lower pressure the separatrix still exists (Fig. 3(c)), but the stable node in the region of high ETBE mole fraction has moved to the composition 0.78ETBE, 0.19EtOH and 0.03IB. In contrast to this, at $p = 1.0$ MPa the lower stable node and the saddle have already extinguished each other. Consequently all trajectories run into the only remaining stable point, pure EtOH.

At Da $= 1$ (Fig. 3(e) and (f)), REA is "strong" in comparison with the separation vector SEP. Therefore every trajectory moves to the line of chemical equilibrium and remains close to this line until the EtOH vertex is reached. The larger the relationship between the lengths of REA and SEP, the more similar the shape of the residue curves discharging into the chemical equilibrium to the shape of straight lines of stoichiometry, see Fig. 3(f).

The results of Fig. 3 can be summarized in the following statements.

• With a given operating pressure $p$, it is possible that one saddle point (equal to the binary azeotropic point between ETBE and EtOH for Da $= 0.0$) and one stable node extinguish each other, if the Damköhler number Da is adequately high. The crucial value of Da, at which this phenomenon occurs, depends on $p$. Hence one stable node in the region of the ETBE vertex disappears and every trajectory ends at pure EtOH.

• The second effect of raising Da is that the collecting trajectory approximates to the curve of chemical equilibrium, and the residue curves running into the collecting trajectory achieve the shape of straight lines of stoichiometry.

• Increase of the operating pressure $p$ means that the discussed effects take place at a lower Damköhler number Da.

## 5. Discussion

First of all, we will discuss the influence of operating pressure $p$ on residue curve maps. With the assumption that the
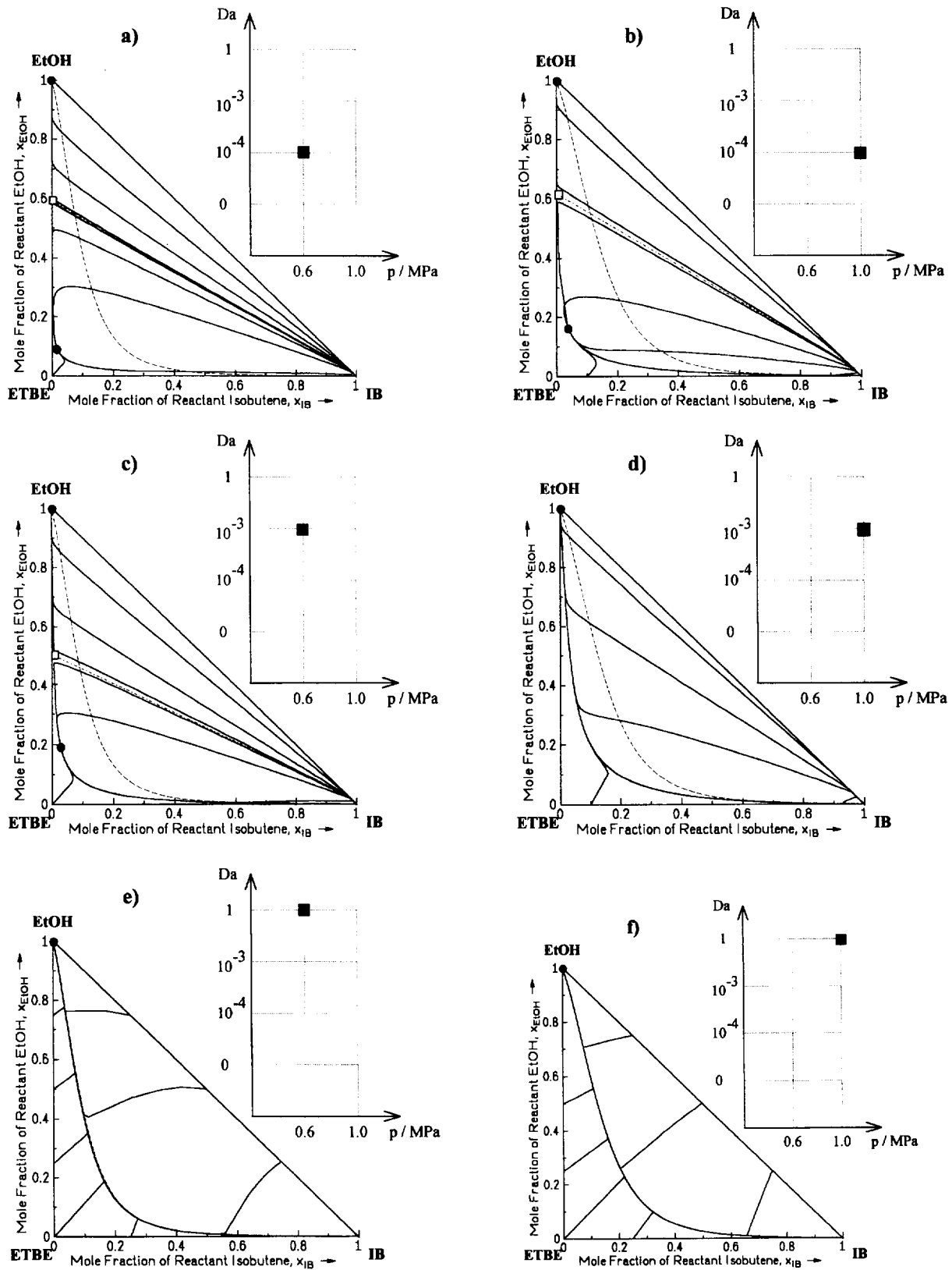
Fig. 3. Residue curve maps for reactive distillation at operating pressure Ip = 0.6 and 1.0 MPa; Damköhler number Da = $10^{-4}$, $10^{-3}$ and 1.

liquid phase is in a state of boiling, a rise in pressure leads to an increase in boiling temperature $T^b$. As shown in the previous section, the reaction rate constant of ETBE synthesis $k_f$ increases exponentially with increasing temperature. Conse-

quently the amount of *REA* grows, whereas *SEP* remains approximately constant. So the enhancement of pressure has nearly the same effect as the enhancement of the Damköhler number Da.
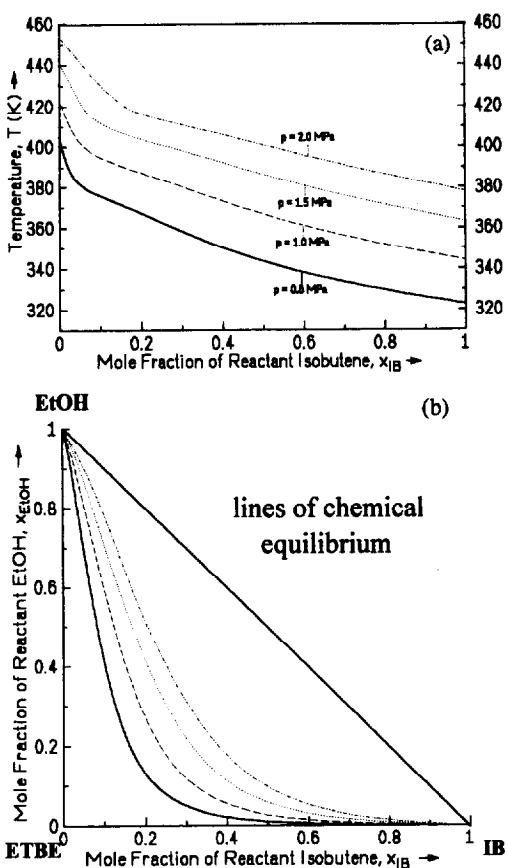
Fig. 4. Profile of boiling temperature along the lines of chemical equilibrium as function of pressure $p$.

In a previous work, it was shown that in the example of TAME synthesis, the occurrence of a second saddle point in the topology is possible at a certain combination of Damköhler number Da and operating pressure $p$ [1]. This phenomenon was explained physically and it could be shown that the existance of a minimum in the temperature profile along the line of chemical equilibrium is a necessary condition.

The shape and location of these profiles is influenced by the operating pressure $p$, which can be established by the following considerations. Raising the pressure leads to an enhancement of the temperature in the still, for the reasons given above. Because of the exothermic characteristic of the ETBE synthesis, the line of chemical equilibrium (CE) is shifted towards the reactants EtOH and IB. If there is a pronounced minimum binary azeotropic point between EtOH and IB, this point will have an influence on the shape of the temperature profiles, so that at a sufficiently high pressure, a minimum in this profile is possible. Hence the temperature profile along the line of chemical equilibrium is an indicator of the possibility of the existence of an additional saddle point. Fig. 4 shows these profiles as a function of pressure $p$. It can be noticed that the temperature increases monotonously from pure IB (r.h.s. of Fig. 4(a)) to pure EtOH (l.h.s. of Fig. 4(a)), independent of operating pressure $p$. Consequently it can be concluded that the existence of an extra fixed

point in the reactive mixture EtOH/ETBE/IB can be excluded.

Another topic to discuss is the existence and position of steady state solutions in the residue curve maps. As already mentioned, these points depend on Da and $p$. To study this dependence, one has to adjust the right hand sides of the set of equations (Eqs. (21)) to zero

$$\underline{0} = f(x, T, \mathrm{Da}) \qquad (23)$$

In this case $f$ is a four-dimensional vector, including five unknown variables $x_{IB}$, $x_{EtOH}$, $x_{ETBE}$, $T$ and Da, with the condition that $p$ is assumed to be constant. To solve Eq. (23), the continuation program PITCON, developed by Rheinboldt and Burkardt [18,19], is applied. To use this method, one has to begin the computation by specifying an approximate initial solution, and subsequent points returned by PITCON lie on the curve which passes through this initial point and is implicitly defined by $f = \underline{0}$. The extra degree of freedom is analogous to the role of the independent variable in differential equations.

The chosen initial solution is the ETBE vertex in the absence of chemical reaction, which is known to be a stable node

$$x_{EtOH} = 0.0; \quad x_{IB} = 0.0; \quad x_{ETBE} = 1.0;$$

$$T = T^b_{ETBE}(P); \quad \mathrm{Da} = 0.0 \qquad (24a,b,c,d,e)$$

The results computed at $p = 0.1, 0.4$ and $0.8$ MPa are shown in Fig. 5. On the left hand side of this figure, the trajectories of steady state are plotted. It can be observed that a stable node branch beginning from pure ETBE moves away from the ETBE vertex with rising Da. As the maximum Damköhler number $\mathrm{Da}_{max}$ is reached, the stable node branch turns into a saddle branch. This point is called the *kinetic tangent pinch* [4]. The saddle branch arrives at $\mathrm{Da} = 0.0$ in the binary azeotropic point between EtOH and ETBE. The kinetic tangent pinches calculated at different operating pressures $p$ are connected with the so-called *branch of kinetic tangent pinches*.

On the right hand side of Fig. 5, the appropriate profile of temperature along the steady state trajectories is plotted. This plot shows the necessary physical condition for the existence of a kinetic tangent pinch, i.e. the presence of a minimum along the trajectory of steady states.

To prove that the discussed node–saddle bifurcation results in a kinetic tangent pinch, a transformation of coordinates is taken through, according to Barbosa and Doherty [20,21]. The new composition variables are

$$X_{EtOH} \equiv \frac{x_{EtOH} + x_{ETBE}}{1 + x_{ETBE}},$$

$$X_{IB} \equiv \frac{x_{IB} + x_{ETBE}}{1 + x_{ETBE}}, \qquad \sum_{i \neq ETBE} X_i = 1 \qquad (25a,b,c)$$
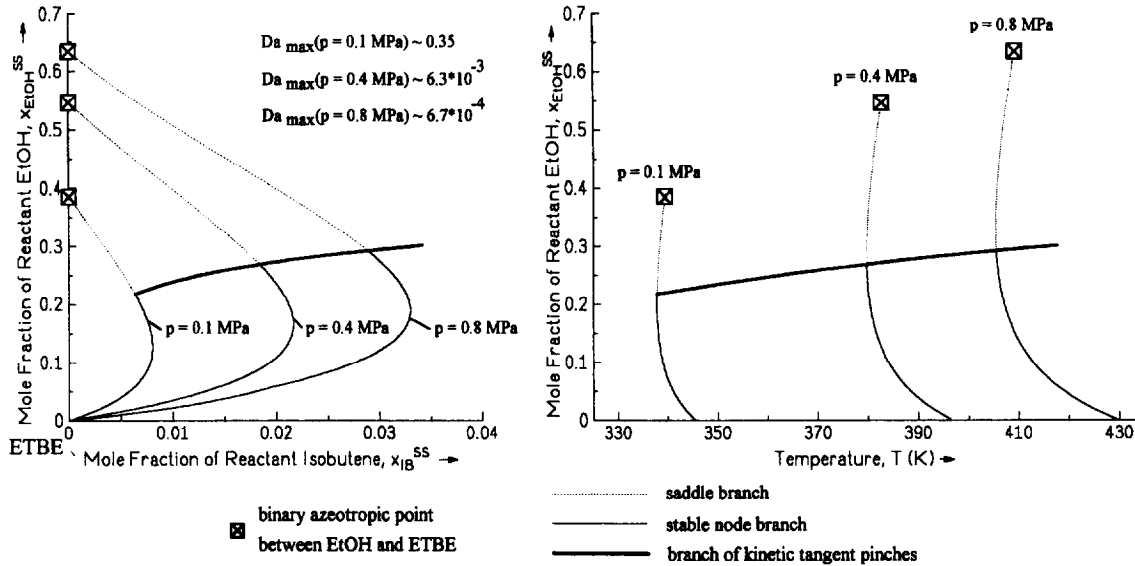
Fig. 5. Steady state solutions of residue curve maps at operating pressure $p = 0.1$, $0.4$ and $0.8$ MPa with branch of kinetic tangent pinches and appropriate profile of temperature.

$$Y_{EtOH} \equiv \frac{y_{EtOH} + y_{ETBE}}{1 + y_{ETBE}},$$

$$Y_{IB} \equiv \frac{y_{IB} + y_{ETBE}}{1 + y_{ETBE}}, \qquad \sum_{i \neq ETBE} Y_i = 1 \qquad (26a,b,c)$$

Furthermore the kinetically limited collecting trajectories are calculated for several Damköhler numbers at fixed pressure using the relationship

$$\underline{0} = REA + SEP_{REA} \qquad (27)$$

The appropriate reactive phase diagrams at $p = 0.8$ MPa calculated for significant Damköhler numbers are shown in Fig. 6. The temperature profile of nonreactive distillation ($Da = 0.0$) plotted in Fig. 6(a) has two extrema; one maximum at pure ETBE (stable node) and one minimum at the binary azeotrope between EtOH and ETBE (saddle point). The small composition triangle on the right hand side of this figure shows the curvature of this line, plotted in "real" liquid mole fractions. The appropriate vapour mole fraction profile is depicted in Fig. 6(b). This shows that these two points fulfil the conditions for azeotropy, formulated by Barbosa and Doherty [21]

$$X_i = Y_i, \ i \neq ETBE \qquad (28)$$

For large Damköhler numbers ($Da \gg 1$), the plot coincides with the line of chemical equilibrium (CE). As already discussed, this curve has no extrema and consequently no reactive azeotropic point.

At the crucial Damköhler number $Da = 6.7 \times 10^{-4}$ (see Fig. 5), the temperature profile shows a saddle at $X_{IB} = 0.38$, which is equivalent to a tangent point on the $Y_{IB} = X_{IB}$ line in Fig. 6(b). Consequently the nomenclature *kinetic tangent pinch* is obvious.

To calculate the branch of kinetic tangent pinches, the set of nonlinear algebraic equations Eq. (23) has to be extended by the equation

$$0 = f_5 = \det(J) = \begin{vmatrix} \dfrac{\partial f_1}{\partial x_{EtOH}} & \cdots & \dfrac{\partial f_1}{\partial T} \\ \vdots & & \vdots \\ \dfrac{\partial f_4}{\partial x_{EtOH}} & \cdots & \dfrac{\partial f_4}{\partial T} \end{vmatrix} \qquad (29)$$

Therefore the dimension of the set of equations $f$ has increased to five, and PITCON computes the six unknown variables $x_{EtOH}$, $x_{IB}$, $x_{ETBE}$, $T$, Da and $p$, which characterize this branch of steady state solutions.

Fig. 7 shows the branch of kinetic tangent pinches plotted as function of $p$ and Da. This plot divides the plane of pressure $p$ and Damköhler number Da into two areas: one region lies above the curve, where the residue curve maps have one stable node at pure EtOH; the other region is located below the plot, and with this combination of $p$ and Da, the residue curve maps have two stable nodes: one node near the ETBE vertex and the other at pure EtOH.

Eq. (30) describes the appropriate mathematical relationship between reciprocal operating pressure $1/p$ and Damköhler number Da for the plotted branch in an interval between $p = 0.1$ and $1.0$ MPa. This equation was found by a least-square interpolation of the numerical solution given by PITCON

$$Da = \ln(1 - 1.819 \cdot 10^{-3}(1/p) + 3.202$$
$$\cdot 10^{-3}(1/p)^2 - 2.132 \cdot 10^{-3}(1/p)^3 + 8.798 \qquad (30)$$
$$\cdot 10^{-4}(1/p) - 1.061 \cdot 10^{-4}(1/p)^5)$$

To summarize, with a given Da and $p$ one is able to predict how many stable nodes will exist in residue curve maps for ETBE synthesis, according to the following criterion:
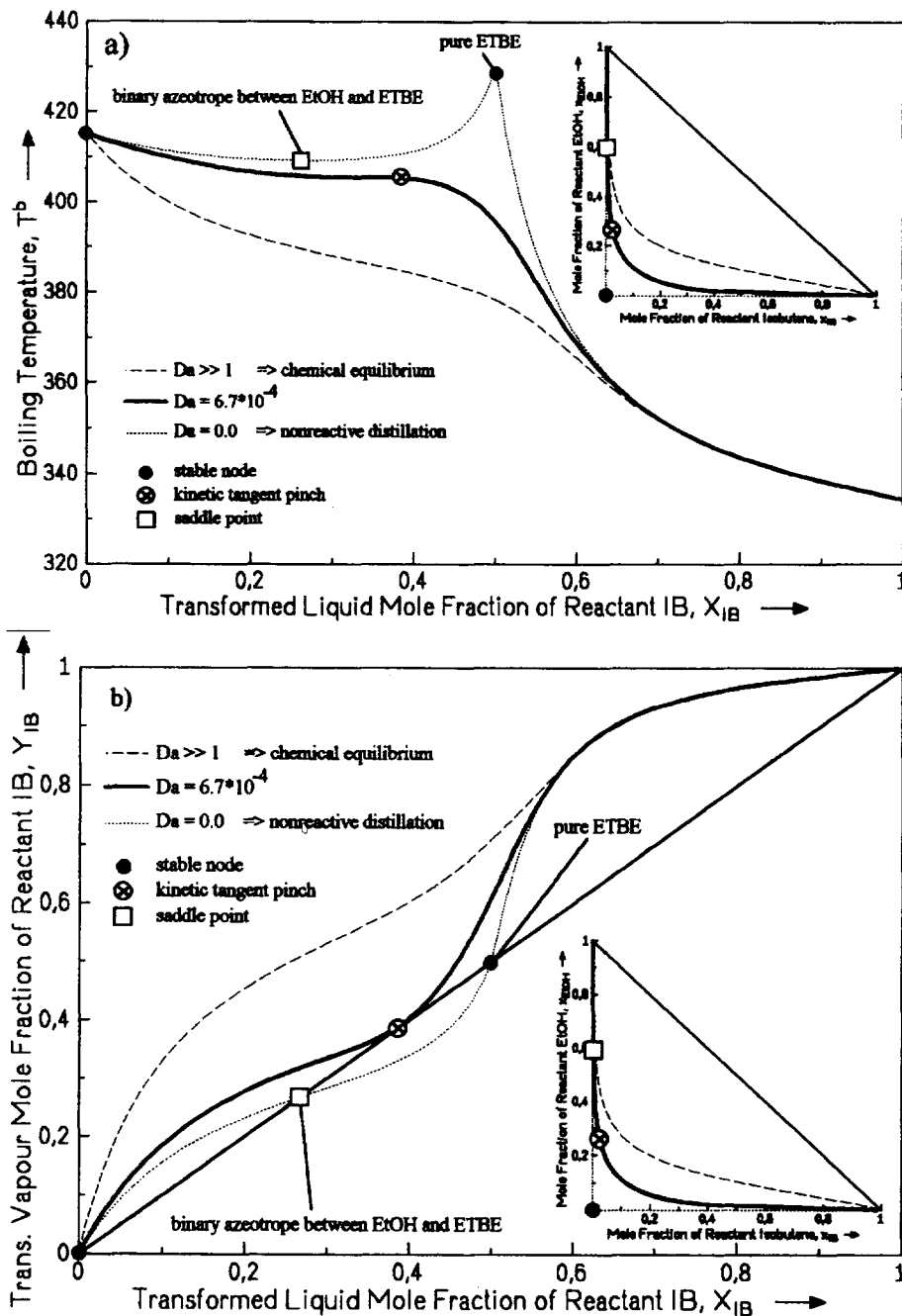
Fig. 6. Phase diagram in transformed coordinates for different Da and fixed pressure $p = 0.8$ MPa: (a) $T^b$–$X_{IB}$ plot, (b) $Y_{IB}$–$X_{IB}$ plot.

$\ln(1 - 1.819 \cdot 10^{-3}(1/p) + 3.202 \cdot 10^{-3}(1/p)^2 - 2.132 \cdot 10^{-3}(1/p)^3$
$+ 8.798 \cdot 10^{-4}(1/p)^4 - 1.061 \cdot 10^{-4}(1/p)^5) - \text{Da} > 0$

$\Rightarrow$ Two stable nodes in the system: near ETBE, and pure EtOH

$\ln(1 - 1.819 \cdot 10^{-3}(1/p) + 3.202 \cdot 10^{-3}(1/p)^2 - 2.132 \cdot 10^{-3}(1/p)^3$
$+ 8.798 \cdot 10^{-4}(1/p)^4 - 1.061 \cdot 10^{-4}(1/p)^5) - \text{Da} < 0$

$\Rightarrow$ One stable node in the system: pure EtOH

## 6. Conclusions

In the present paper, a model has been derived to calculate residue curve maps for simple reactive distillation processes of heterogeneously catalysed etherifications on the basis of

the synthesis of ETBE from EtOH and IB. The heating strategy, which has an effect on the qualitative structure of the model and its solution curves [4], was so chosen that the quotient of vapour flow rate $V$ to liquid holdup $H$ is independent of time.
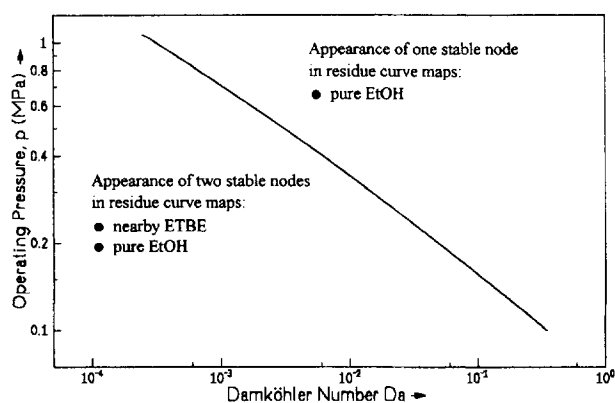
Fig. 7. Plot of the branch of kinetic tangent pinches as functions of $p$ and Da.

Residue curve maps generated by this model can be described by two independent parameters, the Damköhler number Da and the operating pressure $p$.

The Damköhler number considers the relation between the time constant of mass removal via distillation to the time constant of chemical reaction. In practice, Da can be varied either by variation of the mean residence time $H/\dot{V}$ in the still, or by changing the ion exchange capacity of the catalyst. Therefore, Da characterizes the time constant of chemical reaction compared with the time constant of distillation. It has been shown that with increasing Da the collecting line of residue curves approaches the line of chemical equilibrium CE. In addition, the shape of the starting trajectories becomes more similar to the stoichiometrically dominated trajectories.

The operating pressure $p$ effects the boiling temperature $T$ in the still. Increasing $p$ has two consequences. On the one hand, because of the exothermic character of etherifications, the line of CE moves to compositions with little mole fraction of ether. On the other, the length of REA relative to SEP grows, caused by the increasing rate constant of reaction, so that enhancement of $p$ has qualitatively the same effect as an increase in Da.

The simulation of the heterogeneously catalysed synthesis of ETBE shows that at above a certain combination of Damköhler number Da and operating pressure $p$, the number of stable nodes is reduced from two to one. To study the appearance of fixed points, the branches of steady state solutions of residue curve maps were investigated and the fact that the node–saddle bifurcation results in a tangent pinch was demonstrated.

The branch of kinetic tangent pinches was calculated using a continuation method, and the results were discussed with regard to the number of stable nodes.

## Acknowledgements

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