

Residue curve maps of ethyl acetate synthesis reaction

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Abstract: The residue curve maps are considered as a powerful tool for the preliminary design of reactive distillation. The residue curve maps of ethyl acetate synthesis reaction were calculated based on the pseudo-homogeneous rate-based kinetic model and the NRTL activity coefficient model. The results show that the unstable node branch emerges from the ethyl acetate/water edge, moving toward the chemical equilibrium surface with the increase of Damköler value (D), and the node reaches the ternary reactive azeotrope when $D \rightarrow \infty$ eventually. Conceptual design for the ethyl acetate synthesis of reactive distillation based on the residue curve maps is presented at last.

Key words: residue curve maps; ethyl acetate; esterification; conceptual design

1 Introduction

Ethyl acetate (EtAc) is mainly used as solvent in paints and coatings industry, inks production and as industrial solvent in many other branches of industry [1–3]. The most common procedure for producing EtAc was presented in a simple esterification reactor of ethanol (EtOH) with acetic acid (HAc) in the presence of acidic catalyst. However, one of the key issues in the production of EtAc was the equilibrium limitation from the reversible reaction of HAc and EtOH. In order to break the equilibrium limitation and achieve a high conversion, the reactive distillation (RD), which contained reaction and separation in a column simultaneously, became an interesting alternative to produce EtAc. However, most of these RD processes were short of feasibility analysis methodologies due to their complexity. For the conceptual design of the RD process, residue curve maps (RCMs) were introduced as a very useful tool. RCMs have been successfully applied to the complex non-ideal RD systems. In addition, RCMs are based only on the physical properties of system: vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE) and solubility data [4–6]. The RCMs have following characteristics generally:

1) The pathway of the RCMs is only with an outset liquid phase composition, but does not interact with other lines.

2) The RCM lines point to the high boiling point

composition generally.

3) The RCMs only relate with VLE with a known pressure, and the volume has no influence on it.

In the past decade, investigations on RCMs for different systems have been reported. HUANG et al [7] investigated the RCMs of propyl acetate synthesis reaction. Through measuring the compositions around the unstable node, the existence of the reactive azeotrope was verified, and they also found that different heating policies would influence the singular points, and the topology of kinetically controlled RCMs, but not in the cases when Damköler value $D=0$ or $D=\infty$. SANCHEZ-DAZA et al [8] described a calculation procedure of the RCMs using a methodology based on the element concept instead of the usual molar concept. ALMEIDA-RIVERA et al [9] analyzed the homogeneous reactive distillation synthesis of methyl tert-butyl ether from isobutene and methanol at 1.11 MPa using the RCMs. DUARTE et al [10] investigated the effects of adsorption on RCMs for heterogeneous catalytic distillation systems. The influences of D , and the temperature on the adsorptive models were carried out, and they found that the effects of adsorption increased with the increase of D (the ratio of vapor flow rate to liquid holdup) and the temperature.

In the RCMs, temperature always increases along with the residue curve line, and the singular points are the stable nodes, unstable nodes and saddle nodes. This information allows us to assign the RCMs topology for the whole composition space, and makes RCMs a

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promising technique in increasing the productivity. The purpose of this work was to calculate the RCMs of EtAc synthesis reaction, and the conceptual design of the reactive distillation process was also presented based on the analysis of the RCMs.

2 Theory

2.1 Reaction scheme and model equations of RCMs

The esterification reaction of HAC with EtOH is as follows:

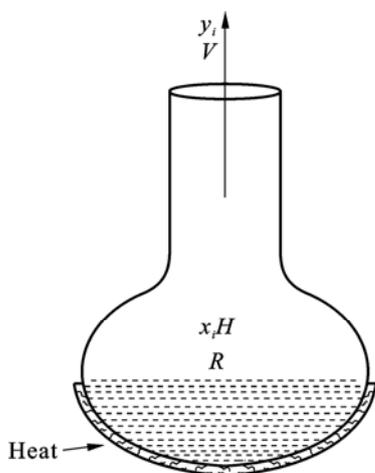


Fig. 1 Simple batch distillation set-up for experimental determination of RCMs

Considering the batch reactive separation process depicted in Fig. 1, mixtures of different initial compositions of the liquid phase and the catalyst were added into the reactor to determine the residue curve maps. The reactor was heated up to the set temperature. The liquid compositions were measured by taking samples from the reactor. When the liquid residue amount was too small to take any more samples, this run was ended. The mass balance of simple batch distillation without the reaction is shown as follows:

$$\frac{dH}{dt} = -V \quad (2)$$

$$\frac{d(Hx_i)}{dt} = -Vy_i \quad (3)$$

$$\frac{dx_i}{dt} = \frac{V}{H} (x_i - y_i) \quad (4)$$

$$\frac{dx_i}{d\xi} = x_i - y_i \quad (5)$$

where x_i and y_i are the mole fractions of component i in liquid and vapor phase, respectively; R denotes the

dimensionless reaction rate depending on the liquid phase composition; H is the liquid volume; V is the evaporation rate; ξ stands for the dimensionless time with $d\xi = (V/H)dt$. The RCMs with reactions can be shown as follows [7]:

$$\frac{dx_i}{d\xi} = x_i - y_i + \frac{H}{V} (v_i - v_{T,x_i}) k_f \left(\prod_{r=1}^{c_r} a_r^{|\nu_r|} - \frac{1}{K} \prod_{p=1}^{c_p} a_p^{|\nu_p|} \right) \quad (6)$$

where v stands for the stoichiometric coefficient of the reaction; K is the reaction equilibrium constant; k_f is the forward reaction rate constant; c_r and c_p are the quantities of reactant and product, respectively. In the following, two parameters are introduced to formulate Eqs. (7) and (8) in a comprehensive way. These are the Damköler number (D) and R :

$$R = \frac{r}{k_f} = \prod_{r=1}^{c_r} a_r^{|\nu_r|} - \frac{1}{K} \prod_{p=1}^{c_p} a_p^{|\nu_p|} \quad (7)$$

$$D \equiv \frac{H_0/V_0}{1/k_{f,\text{ref}}} \quad (8)$$

Thus, Eq. (6) could be rewritten as

$$\frac{dx_i}{d\xi} = x_i - y_i + \frac{H}{V} \frac{V_0}{H_0} (v_i - v_{T,x_i}) \frac{k_f}{k_{f,\text{ref}}} DR \quad (9)$$

Supposing that the heating strategy can meet $\frac{V}{H} = \frac{V_0}{H_0} = \text{const.}$ and the system is pseudo-homogeneous, Eq. (9) can be rewritten as

$$\frac{dx_i}{d\xi} = x_i - y_i + (v_i - v_{T,x_i}) \frac{k_f}{k_{f,\text{ref}}} DR \quad (10)$$

Equation (10) will be used to study the RCMs of EtAc synthesis reaction by reactive distillation.

2.2 Kinetic model

The kinetics of HAC with EtOH catalyzed by Amberlyst-36Wet was investigated in our preliminary work [11]. The pseudo-homogeneous kinetic models, Eqs. (11)–(13), have been proposed to explain the reaction. The parameters, namely pre-exponential factors A_+ and A_- , and the energies of activation E_{a+} and E_{a-} are obtained, as given in Table 1.

$$-r_{\text{EtOH}} = -\frac{1}{W_{\text{Cat}}} \frac{dC_{\text{EtOH}}}{dt} = K_+ C_{\text{EtOH}} C_{\text{HAc}} - K_- C_{\text{EtAc}} C_{\text{Water}} \quad (11)$$

$$K_+ = A_+ \exp\left(\frac{E_{a+}}{RT}\right) \quad (12)$$

$$K_- = A_- \exp\left(\frac{E_{a-}}{RT}\right) \quad (13)$$

Table 1 Pre-exponential factors and activation energy

Reaction	$A/(L \cdot mol^{-1} \cdot min^{-1} \cdot g^{-1})$	$E_a/(kJ \cdot mol^{-1})$
Forward	131 137	57.96
Reverse	81 389	60.55

2.3 Vapor–liquid equilibrium

The mole fraction y_i can be calculated as

$$y_i p = \gamma_i x_i p_i^{\text{sat}} \quad (14)$$

where p is the pressure; x_i and y_i are the mole fractions of component i in liquid and vapor phases, respectively; γ_i is the liquid phase activity coefficient calculated by the NRTL model (Eq. (16)). According to the parameters displayed in Table 2, the saturated pressures could be calculated by the Antoine equation:

$$p_i^{\text{sat}} = \exp\left(a + \frac{b}{T+c} + d \times T + e \times \ln(T) + f \times T^g\right) \quad (15)$$

where p_i^{sat} is the saturated pressure (Pa), and T is the absolute temperature (K).

The NRTL activity coefficient model could be used in the partly soluble system, and the budget precision

was high. So, the NRTL activity coefficient model was used to compute the liquid phase activity quotient in this work, and the parameters are displayed in Table 3. The boiling points and compositions of the azeotropic mixtures were calculated at atmospheric pressure, as given in Table 4.

$$\ln \gamma_i = -\frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{kj}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_j x_k G_{kj}} \right] \quad (16)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}); \quad G_{ii} = 0$$

$$\tau_{ij} = \frac{A_{ij}}{RT} + B_{ij}; \quad \tau_{ii} = 1$$

2.4 Equilibrium constant

The aspect of the reaction was completed by calculating the chemical equilibrium constant for the multi-component vapor–liquid mixtures. The k_{eq} is the chemical equilibrium constant for the reaction, which is calculated by

$$k_{\text{eq}} = \prod_{i=1}^{i=n} (\gamma_i \cdot x_i)^{\nu_i} = f(x_i, \gamma_i(x_i, T)) \quad (17)$$

Table 2 Parameters of Antoine equation [12]

Component	a	b	c	$d/10^{-3}$	e	$f/10^{-17}$	g
EtOH	81.075 3	-7 827.801 3	0	1.858 6	-7.961 3	2.367 3	6
HAc	30.553 1	-5 699.312 2	0	5.411 8	-0.396 5	8.065 1	6
EtAc	76.015 7	-6 456.268 8	0	2.840 2	-8.035 9	1.469 9	6
H ₂ O	65.154 4	-6 842.907 3	0	2.783 5	-6.136 4	3.311 7	6

Table 3 Parameters of NRTL activity coefficient model

Component i	HAc	HAc	HAc	EtOH	EtOH	EtAc
Component j	EtOH	EtAc	H ₂ O	EtAc	H ₂ O	H ₂ O
A_{ij}	-252.482	-235.278 9	609.888 6	-421.289 0	-266.533	1 290.464 0
A_{ji}	225.475 6	515.821 2	-723.888 1	1 614.287 3	444.815 7	-4.428 7
B_{ij}	0	0	-1.976 3	1.871 3	0.806 5	-2.345 6
B_{ji}	0	0	3.329 3	-4.412 9	0.514 3	3.853 8
α_{ij}	0.3	0.3	0.3	0.1	0.4	0.364 3

Table 4 Compositions and temperatures of azeotropes at atmospheric pressure

Azeotrope	Data from Refs. [13–15]				Calculated data			
	w(EtOH)/%	w(EtAc)/%	w(H ₂ O)/%	$T/^\circ\text{C}$	w(EtOH)/%	w(EtAc)/%	w(H ₂ O)/%	$T/^\circ\text{C}$
EtOH-H ₂ O	95.5		4.5	78.1	95.9		4.1	78.18
EtAc-EtOH	29.8	70.2		71.8	30.73	69.27		71.43
EtAc-H ₂ O	91.3		8.7	70.9		91.47	8.53	70.37
EtAc-EtOH-H ₂ O	9.8	82.0	8.2	70.23	10.70	81.80	8.53	69.95

3 Analysis of RCMs

D (Damköler number) is an important parameter in the RCMs with reaction, and the value of D stands for the degree of the influences of the reaction on the RCMs. From Eq. (8), D is a ratio of phase equilibrium strength to the reactive equilibrium strength [16]. When the reaction achieves the equilibrium and D achieves the limit value (D_{lim}), there is a balance between the phase equilibrium and the reactive equilibrium. D could not affect the RCMs if its value is larger than D_{lim} , no matter how it increases. In Eq. (10), $D=0$ stands for the state that the system has no reaction; when D approaches to the infinity value (D_{lim}), the system achieves the balance, and when the value of D is between zero and D_{lim} , the system is kinetically controlled.

Figure 2(a) shows the RCMs without reaction at 1.11 MPa. There are one ternary azeotrope and three binary azeotropes in the RCMs. The ternary azeotrope (Az.1) of EtAc/EtOH/H₂O is the unstable node, while the other three azeotropes [EtAc/EtOH (Az. 2), EtOH/H₂O (Az. 3), and EtAc/ H₂O (Az. 4)] are the saddle nodes.

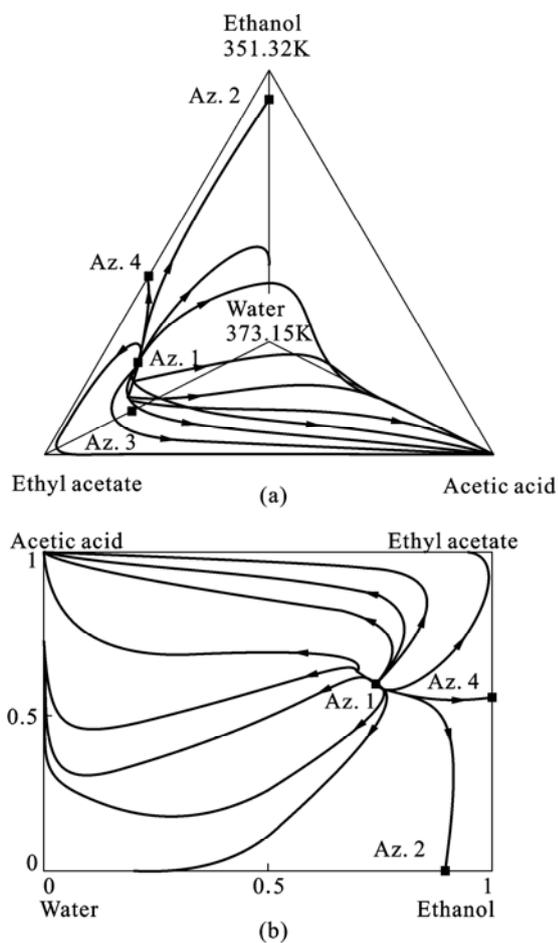


Fig. 2 RCM with $D=0$

Pure EtAc, EtOH and H₂O are also saddle nodes, and HAc is the only stable node for the simple distillation. RCM Pure EtAc, EtOH and H₂O are also saddle nodes, and HAc originates from the unstable node, approaches to the saddle points firstly, and converges to the stable node finally. For better visualization, the RCMs are transformed into the planar graph, as shown in Fig. 2(b) [16].

Under the different values of D , the changes of the RCMs with the same initial liquid compositions are shown in Fig. 3. The adding of the reaction has obvious influence on EtAc/EtOH/H₂O azeotropy compositions, and the reaction azeotrope Az. 11 appears. Meanwhile, the value of D is between 0.1 and 5.0, and the RCMs are completely coincident, which demonstrates that the phase equilibrium strength and the reactive equilibrium strength achieve equilibrium when $D=0.1$.

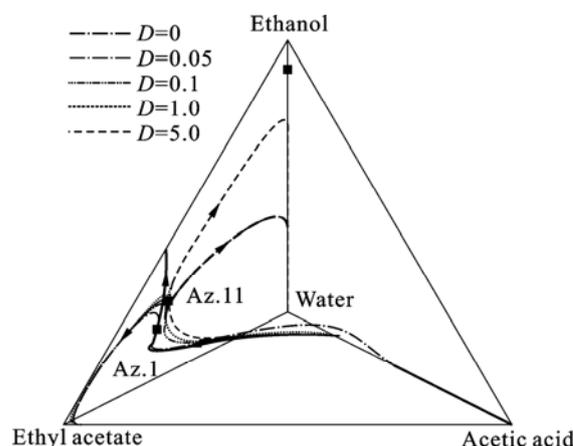


Fig. 3 RCMs with different D values

4 Conceptual design using RCMs

By the analysis of the RCMs and the azeotropic mixtures, HAc is the high boiling point product in the system and should be obtained from the bottom of the RD column. On the contrary, the boiling points of EtAc/H₂O/EtOH, EtAc/H₂O, and H₂O/EtOH azeotropes are close and low, which are obtained as the top product. As mentioned above, when the value of D is 0.1, phase equilibrium strength and the reactive equilibrium strength have achieved equilibrium, which means that the phase equilibrium is the main factor affecting the product's purity. So, high-purity EtAc product ($\geq 99.5\%$) could not be obtained using only one RD column (RDC), and another purification distillation column (PDC) should be added. The schematic diagram of preliminary design for producing EtAc by reactive distillation is shown in Fig. 4. As shown in Fig. 4, HAc and EtOH are fed into the RDC. After reaction and primary purification, a very small quantity of HAc is withdrawn at the bottom

of the RDC. The overhead vapor products are EtAc/H₂O/EtOH, EtAc/H₂O, and H₂O/EtOH azeotropic mixtures which will be condensed to ambient temperature and introduced to a decanter for phase separation. The water formed by the reaction is removed from the phase separator. Part of the organic phase is refluxed back to the RDC, and another part of the organic phase is fed into the PDC. The EtAc product is obtained at the bottom of the PDC. The operating curves for production of EtAc by reactive distillation are presented in Fig. 5. Feedstock F_0 and reflux R_1 (V_2 , B_1 , and L_1) are fed into the RDC. The top product V_1 and bottom product B_1 are obtained after reaction and purification. By the analysis of liquid–liquid phase splitting, adding water contributes to the purification of the two phase, and makes the point V_1 move toward V . Finally, the organic phase is purified by PDC and the high-purity EtAc product is obtained.

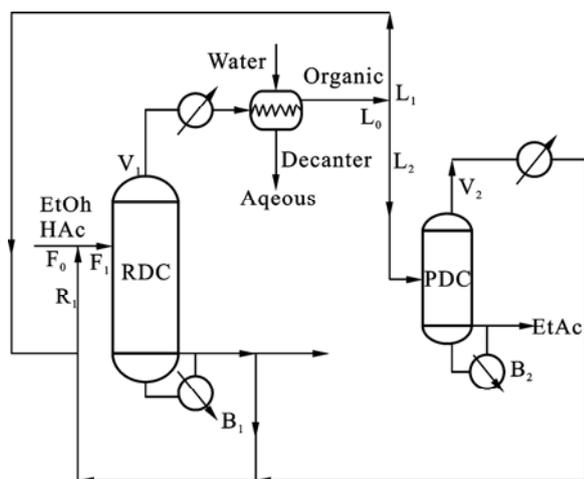


Fig. 4 Schematic diagram of preliminary design for production EtAc by reactive distillation

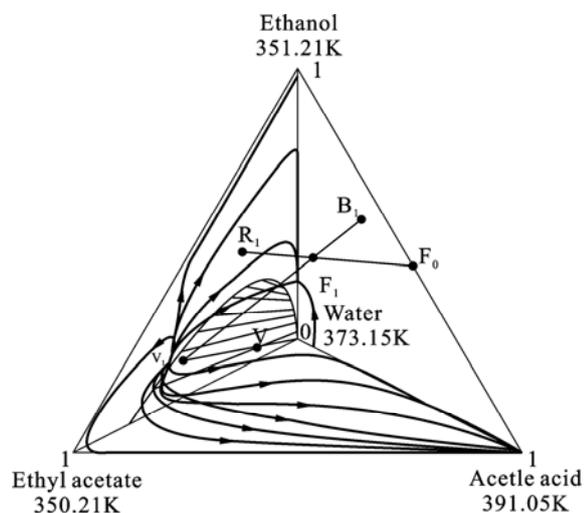


Fig. 5 Operating curve for production EtAc by reactive distillation

5 Conclusions

1) For the conceptual design of the RD process, RCMs are introduced as a very useful tool. The RCMs of the EtAc esterification system are calculated based on the pseudo-homogeneous rate-based kinetic model and the NRTL activity coefficient model.

2) The results show that there are one ternary azeotrope and three binary azeotropes in the RCMs, and the adding of the reaction has obvious influences on the EtAc/EtOH/H₂O azeotropy compositions.

3) The conceptual design for the EtAc synthesis of reactive distillation based on the RCMs is presented, and the high-purity EtAc product is obtained.

Nomenclature

x_i, y_i	Mole fractions of component i in liquid and vapor phase, respectively
R	Dimensionless reaction rate depending on liquid phase Composition
H	Liquid volume
V	Evaporation rate
F_0, F	Feedstock
R_1	Reflux
V_1, V_2, L_0, L_1, L_2	Top product
B_1, B	Bottom product
K	Reaction equilibrium constant
k_f	Forward reaction rate constant
c_r, c_p	Quantities of reactant and product
D	Damköler number
R	Universal gas constant, 8.314 J/(mol·K)
A_+, A_-	Pre-exponential factors
E_{a+}, E_{a-}	Energies of activation
p	Pressure, Pa
p_i^{sat}	Saturated pressure of component i , Pa
T	Temperature, K
G	Parameter for NRTL model
k_{eq}	Chemical equilibrium constant
ζ	Dimensionless time
ν	Stoichiometric coefficient of reaction
γ_i	Activity coefficient of component i
τ, α	Parameters for NRTL model

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