

Simulation of Continuous Esterification Process of Polyester Polyols^{*}

CHEN Like (陈礼科), XI Zhenhao (奚桢浩), QIN Zhen (秦榛), ZHAO Ling (赵玲)** and YUAN Weikang (袁渭康)

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Abstract Based on the kinetic and thermodynamic equations, a comprehensive mathematical model for the continuous esterification process of polyester polyols was developed, which was carried out in an innovational bubbling reactive distillation tower (BRDT) at atmospheric pressure. In this new type of reactor, direct esterification between ethylene glycol and adipic acid was accomplished efficiently and rapidly. A bench BRDT with the height of 2 m was applied for the esterification process of poly (ethylene adipate) (PEA). In the continuous operation, linear oligomers were discharged from the bottom of the column, while water passed a few column trays and a packing section as a condensation byproduct. The influence of major operating conditions on reactor performance was also simulated. Simulation results were in good agreement with experimental data, providing a strategy for developing and optimizing this process.

Keywords poly (ethylene adipate), esterification, continuous operation, mathematical model, reactive distillation

1 INTRODUCTION

Polyester polyols are macroglycols that are prepared by the condensation of a glycol and a dicarboxylic acid or acid derivative *via* batch processes in large-scale operations. Polyester polyols of diverse specification and brands can produce polyurethane products by reaction with isocyanates. Global production capacity for polyurethane gets 17 million metric tons in 2010 [1, 2]. Global demand for polyester polyols grows to 1.52 million metric tons in 2008, corresponding to an average growth of 5.4% per year [3]. In spite of the growing use of poly (ethylene adipate) and other polyester polyols, their continuous esterification technology has not been reported [4].

Processes for the batch preparation of polyester polyols, which are generally configured with stirred tanks, are disclosed in many patents [5, 6]. Batch processes are flexible, producing a variety of brands of polyester polyol products, but the product quality is unstable. Moreover, due to the limited heat and mass transfer, the reaction cycle is particularly long.

Esterification reaction for polyester polyols, from the reaction of two functional groups, is usually a reversible endothermic reaction with the formation of volatile byproducts [7, 8]. The reaction and devolatilization are coupled in the esterification process. In order to remove byproduct from the polymeric solution effectively, the esterification apparatus should provide sufficient heat exchange and separation effect. A heated counter-current sieve plate distillation column was used in continuous preparation of polyester prepolymer with the steps of esterifying unreacted acid and hydroxyl end groups [9]. In the heated column reactor, the reactants continuously flowed across multiple reactor plates, while inert gas flowed upward through the column reactor. The residence time for reaction was about 3 min.

The reactor had no agitation. However, its operating flexibility was unsatisfactory, because of weeping or entrainment flooding.

In this study, an innovational bubbling reactive distillation tower (BRDT) reactor [10] is used for bulk esterification reactions. The BRDT contains several reaction trays with special construction and a section with packings. In the process, molten linear oligomers flow through each tray from the top to the bottom by gravity, without agitation, and are discharged from the bottom of the column, while water passes the trays and packing section from the bottom to the top as a condensation byproduct. The flowing fluid on the trays has little dead zone due to the intensive bubbling effect of water, ethylene glycol (EG) vapor and inert gas nitrogen, ensuring their optimum intermixing. In this study, a comprehensive mathematical model for the continuous esterification process of poly (ethylene adipate) (PEA) in the BRDT is developed. The influences of operating conditions on reactor performance are investigated.

2 ASSUMPTIONS AND MODELING

2.1 Polymer segment approach

In a polymerization process, polymers form in varying chain lengths. A modeling approach that properly accounts for varying chain lengths is important to establish the framework for representing polymers in the reaction kinetics. There are two approaches: molecular species models and functional group models. Generally speaking, molecular species models are more comprehensive than functional group models in providing the information of product composition, but much more time is required for the calculation, because each unique polymer molecule is tracked as an independent

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^{**} To whom correspondence should be addressed. E-mail: zhaoling@ecust.edu.cn

component. In this study, the polymer segment approach [11], which is a functional group approach, is used to establish the overall reaction network.

Polymerization can be regarded as reactions between two reactive functional groups. The components in this reaction scheme are EG, adipic acid (AA), T-EG, T-AA, B-EG, B-AA, and water (W). Here, we define four different oligomeric segments: T-EG, T-AA, B-EG, and B-AA, where T and B represent terminal functional group and bound monomer repeating units, respectively.

Using the polymer segment approach, the acid value ([H]) and hydroxyl value ([OH]) of the oligomers can be written as

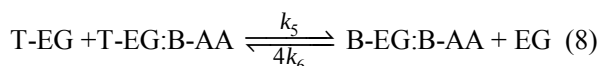
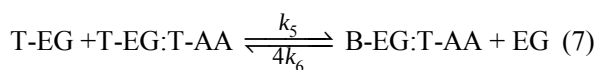
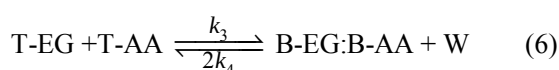
$$[H] = 2 \times [AA] + [T-AA] \quad (1)$$

$$[OH] = 2 \times [EG] + [T-EG] \quad (2)$$

The esterification degree (E_s) expresses the extent of reaction in the continuous esterification process, which can be given by converting acid value and hydroxyl value [12].

2.2 Reaction scheme

There are two primary reactions in PEA polymerization: esterification (or water formation) and condensation (or transesterification) [13]. Assuming that the reactivity of functional group does not depend on the polymer chain length [14, 15], the complete set of reaction is written as [16]



T-EG can be covalently bonded to either a T-AA segment or a B-AA segment. We can write [T-EG:T-AA] as the probability of finding a T-EG segment connected to T-AA. The associated reaction rates for these 6 reactions are

$$R_1 = 4k_1c_1c_2 - k_2c_3 \frac{c_4}{c_4 + c_6} c_7 \quad (9)$$

$$R_2 = 2k_1c_1c_4 - 2k_2c_3 \frac{c_6}{c_4 + c_6} c_7 \quad (10)$$

$$R_3 = 2k_3c_3c_2 - 2k_4c_5 \frac{c_4}{c_4 + c_6} c_7 \quad (11)$$

$$R_4 = k_3c_3c_4 - 2k_4c_5 \frac{c_6}{c_4 + c_6} c_7 \quad (12)$$

$$R_5 = k_5c_3c_3 \frac{c_4}{c_4 + c_6} - 4k_6c_5 \frac{c_4}{c_4 + c_6} c_1 \quad (13)$$

$$R_6 = k_5c_3c_3 \frac{c_6}{c_4 + c_6} - 4k_6c_5 \frac{c_6}{c_4 + c_6} c_1 \quad (14)$$

where c_i represents the concentrations of components in the reaction mixture, numbers 1–7 denote EG, AA, T-EG, T-AA, B-EG, B-AA, and W, respectively.

For a simulation of esterification process, the rate constant k_i ($i = 1-6$) and equilibrium constant K_i ($i = 1, 2, 3$) should be determined. From previous work [12], it can be assumed that the reactivities of acid end group on AA and on polymer chain are the same while the reactivities of hydroxyl end group on EG and on half-esterified EG are different. The rate constants depend on temperature according to the Arrhenius equation

$$k_i = k_{0i} \exp\left(\frac{-E_{ai}}{RT}\right) \quad (\text{for } i = 1, 3, 5) \quad (15)$$

where k_{0i} is the preexponential factor ($\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$), E_{ai} is the activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), R is the gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is the temperature (K). The kinetic and thermodynamic parameters are given in Table 1.

Table 1 Kinetic and thermodynamic parameters [17, 18]

No.	$k_0/\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$	$E_a/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta H/\text{J} \cdot \text{mol}^{-1}$
k_1	1.14×10^4	42.8		
k_3	2.46×10^5	54.6		
k_5	2.24×10^5	60.1		
K_1			43.2	1.58×10^4
K_2			50.4	2.01×10^4

The complete set of reaction considered here is a reversible equilibrium reaction [19, 20], with $k_2 = k_1/K_1$, $k_4 = k_3/K_2$, and $k_6 = k_5/K_3$. For the temperature range considered, entropy and enthalpy change are constant in accordance with the thermodynamic equation [21, 22]:

$$K_i = \exp\left(\frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT}\right) \quad (\text{for } i = 1, 2) \quad (16)$$

$$K_3 = K_2 / K_1 \quad (17)$$

where ΔS is the entropy change ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and ΔH is the enthalpy change ($\text{J} \cdot \text{mol}^{-1}$).

2.3 Phase equilibrium

For the calculation of concentrations of volatile components (EG and water) in the liquid and vapor phases, a quasi-steady state assumption is used for the

vapor-liquid equilibrium. The vapor-phase calculations for oligomeric components are not considered since the polymer is not volatile. The vapor phase is assumed to follow the ideal gas law:

$$p_i = Py_i \quad (18)$$

where P is the total pressure in the reactor, p_i and y_i are the partial pressure and mole fraction of volatile component i in the vapor phase, respectively. Using Raoult's law, the partial pressure of volatile components is

$$p_i = p_i^* x_i \quad (19)$$

where p_i^* is the saturated vapor pressure (Pa) of volatile component i , and x_i is the mole fraction of component i in the liquid phase. The vapor pressure data of water and EG are obtained from a pure component databank [23, 24].

for EG

$$\ln p_1^* = 79.3 - 10105/T - 7.5 \ln T + 7.3e^{-19}T^6 \quad (20)$$

for water

$$\ln p_7^* = 73.6 - 7259/T - 7.3 \ln T + 4.2e^{-6}T^2 \quad (21)$$

2.4 Mathematical model

Figure 1 is the mathematical model diagram for the BRDT. The six column trays are assumed to be six continuous stirred tank reactors (CSTRs) due to the intensive bubbling effect of water and EG. The material balance equations of each component in a CSTR can be written as

$$mdc_1^0/dt = F^i c_1^i - F^o c_1^o + m(-R_1 - R_2 + R_5 + R_6) - F^V c_1^V + F^R c_1^R \quad (22)$$

$$mdc_2^0/dt = F^i c_2^i - F^o c_2^o + m(-R_1 - R_3) \quad (23)$$

$$mdc_3^0/dt = F^i c_3^i - F^o c_3^o + m(R_1 + R_2 - R_3 - R_4 - 2R_5 - 2R_6) \quad (24)$$

$$mdc_4^0/dt = F^i c_4^i - F^o c_4^o + m(R_1 - R_2 + R_3 - R_4) \quad (25)$$

$$mdc_5^0/dt = F^i c_5^i - F^o c_5^o + m(R_3 + R_4 + R_5 + R_6) \quad (26)$$

$$mdc_6^0/dt = F^i c_6^i - F^o c_6^o + m(R_2 + R_4) \quad (27)$$

$$mdc_7^0/dt = F^i c_7^i - F^o c_7^o + m(R_1 + R_2 + R_3 + R_4) - F^V c_7^V + F^R c_7^R \quad (28)$$

where $c_1^i - c_7^i$ and $c_1^o - c_7^o$ represent the input and output concentrations of components in the reaction mixture, respectively, F^i and F^o represent the input and output flow rates, respectively, m is the mass of liquid phase, F^V and F^R are the vapor flow rate to the distillation column and the reflux flow rate from the column, respectively. For the constant reactor volume, the following relation holds:

$$F^i + F^R = F^o + F^V \quad (29)$$

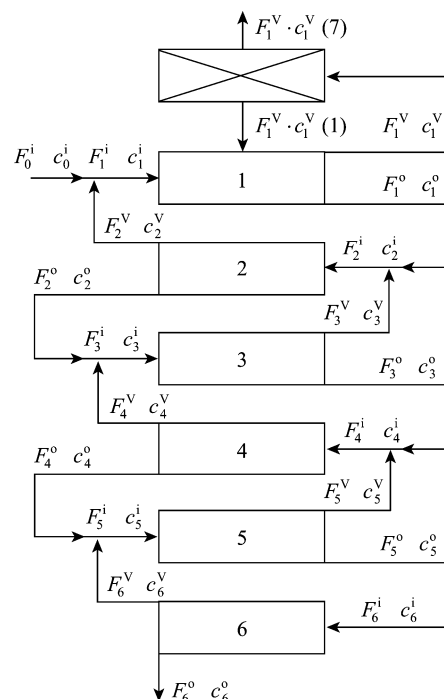


Figure 1 Mathematical model diagram of BRDT

For the first CSTR, it is assumed that all vaporized EG is refluxed and all vaporized water is removed from the distillation column, i.e., $F^V c_1^V = F^R c_1^R$ and $F^R c_7^R = 0$. This perfect separation simplifies the flash calculation with negligible errors. For the next five CSTRs, it is assumed that all vaporized EG and vaporized water are removed from the local distillation column to the above one, i.e., $F^R c_1^R = 0$ and $F^R c_7^R = 0$.

For the steady-state simulation, the differential material balance equations become nonlinear algebraic equations.

3 EXPERIMENTAL

3.1 Materials

AA (>99.5%, AR grade), EG (>99.0%, AR grade) and KOH (>85.0%, AR grade) were supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd. Karl Fisher titration (5 mg water per milliliter) was supplied by Aladdin Industrial Corporation.

3.2 Apparatus and process

The BRDT has three main parts: tower shell, column trays, and packing section, see Fig. 2. Agitation and dynamic packing surface are not needed, avoiding air leakage.

In the operation, a paste of AA and EG is supplied continuously to the first tray of BRDT. Homogeneous melt oligomers from the upper tray to the next one flow on the outer wall, which acts as an additional

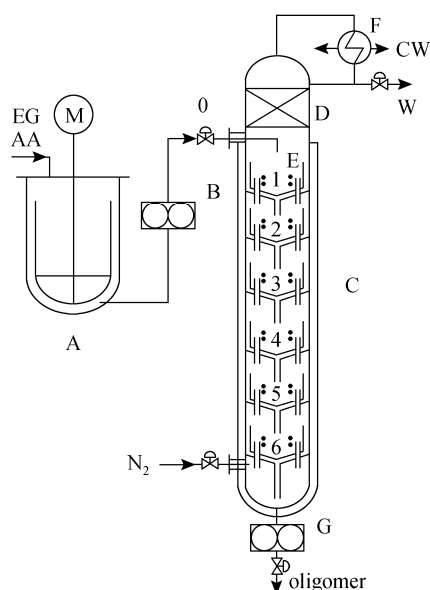


Figure 2 Flow diagram of bench BRDT with slurry kettle (A—slurry kettle; B, G—measuring pump; C—tower shell; D—packing tower; E—column trays; F—condenser; M—motor; CW—condensed water; 0—initial input flow)

evaporation surface, to each tray in a conical shape collector and discharge at the bottom of the cone. Dip pipes introduce the reaction gas and nitrogen to upper trays. This arrangement makes the reaction gas and nitrogen flow counter-currently with the product stream, with gas bubbling through the reaction material and optimum intermixing. The viscosity of the reactants is low, even at the BRDT bottom, the viscosity of the melt product is a few centipoise cP, see Fig. 3. It is easy for gas to pass through the liquid layer. The trays are preferably designed for a residence time of 10 to 40 min in order to achieve desired reaction progress. The reaction gas and nitrogen from the first column tray pass the packing section, water and nitrogen are discharged as byproducts (contain 0.096% EG by mass), while EG is back to the first tray for further reaction. When the esterification process reaches steady state, the concentrations of components in every tray are constant (0 represents initial input flow from the bottom of slurry kettle).

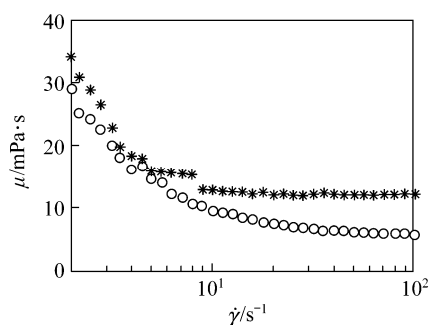


Figure 3 Viscosity of esterification product from BRDT bottom at different temperatures
* 160 °C; ○ 230 °C

This bench BRDT with the height of 2 m was applied to PEA esterification process. The mole feed ratio of EG to AA was 1.2, a paste of which was produced in the slurry kettle maintained at 95 °C and 101.325 kPa. The material from the slurry kettle was supplied continuously to the first tray of BRDT by measuring pump, where the reaction temperature was controlled at 160 °C, which is above the melting point of adipic acid. The temperatures on next 5 trays were controlled at 180 °C, 200 °C, 220 °C, 230 °C, and 230 °C by temperature control devices (see Fig. 4). The homogeneous melt flowed down through 6 trays, and the product was discharged from the reactor by another measuring pump. The residence time on each tray was about 15 min, and the total residence time in BRDT was about 1.5 h. Nitrogen was continuously bubbled through the reactor at 50 ml·min⁻¹ at the bottom of the reactor, and water and nitrogen passed the packing as a condensation byproduct.

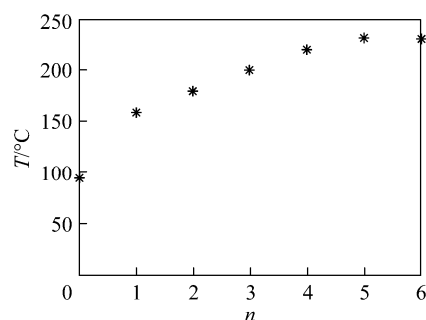


Figure 4 Temperatures controlled at trays

Samples were taken from the bottom of the slurry kettle and every tray when the acid value of product from the bottom of BRDT was constant.

3.3 Sample analysis

The concentration of carboxyl (acid value, [H]) and that of hydroxyl (hydroxyl value, [OH]) were determined from the samples by titration with KOH based on GB/T 2708—1995 and GB/T 2709—1995, respectively. The concentration of water ([W]) was determined by titration with METTLER V20 Karl Fisher Titrator based on GB/T 12008.6—1989. The concentration of free EG ([EG]) was analyzed according to literature [25]. The rheological behavior of esterification product was analyzed by ARES rheometer.

4 RESULTS AND DISCUSSION

4.1 Verification of the model

Simulation results using the reaction rate constants parameters in Table 1 are shown in Figs. 5 and 6. As the reactions proceed, the concentrations of EG and AA decrease, while those of B-EG and B-AA increase. The concentrations of the terminal functional

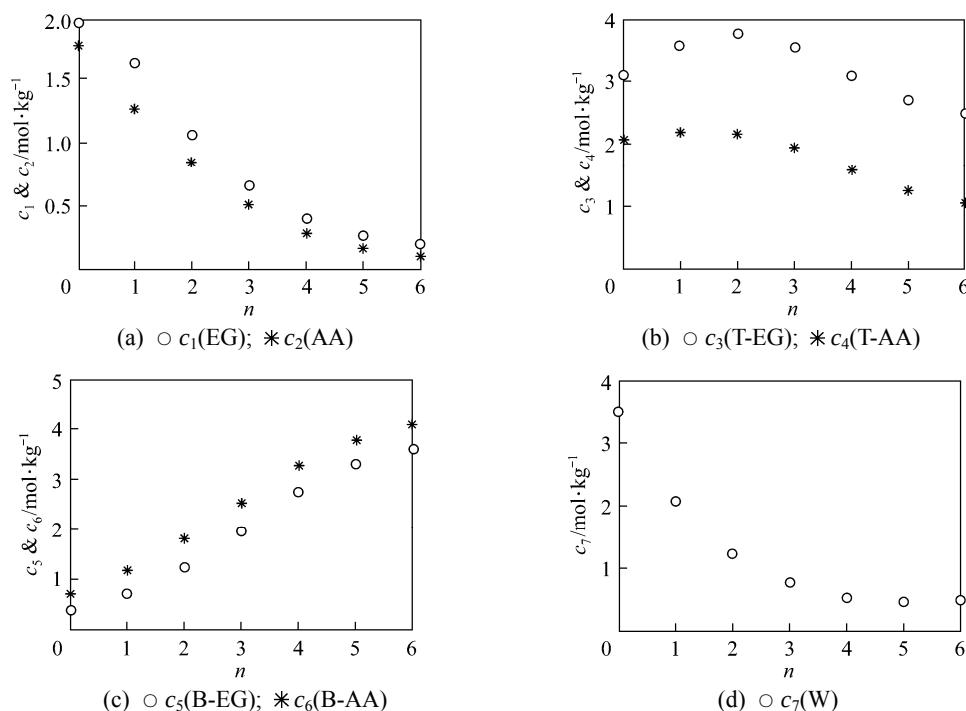


Figure 5 Model outputs for seven components (feed ratio of EG to AA: 1.2; pressure: 101.325 kPa; residence time on each tray: 15 min)

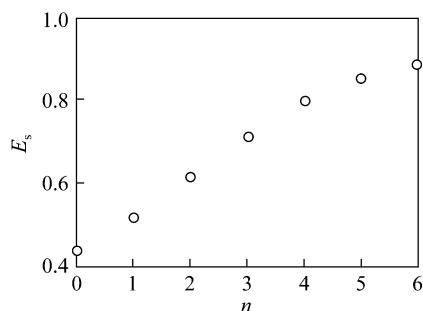


Figure 6 Model outputs for esterification degree (feed ratio of EG to AA: 1.2; pressure: 101.325 kPa; residence time on each tray: 15 min)

groups T-EG and T-AA first increase and then decrease, because the esterification reaction of Eq. (3) is dominant at the beginning and then the esterification reaction of Eq. (6) plays important role. The water gas bubbles through the reaction material from the bottom to the top of column, so that the concentration of water in the reaction system decreases as temperature increases. The esterification degree E_s increases rapidly and a high conversion of AA is achieved in short residence time.

It is desirable to validate the above model equations with experimental data. Fig. 7 shows the comparison of simulated and experimental acid value ([H]), hydroxyl value ([OH]), concentrations of EG ([EG]) and water ([W]). For complicated polymerization reaction systems, it is not easy to obtain all components by

experiment. The calculating results fit experimental data well. The average relative error of this model is anticipated to be smaller than 10%.

4.2 Process simulation

The model for continuous PEA esterification process in BRDT reactor is very useful to predict the reaction results, although it is complicated because of the multi-reactor polymerization. Two of the main objectives in an esterification operation are to achieve high conversion of AA in short residence time and to obtain esterification products with certain hydroxyl value ([OH]). They are polymerized to low acid value ([H]) (less than $0.02 \text{ mol} \cdot \text{kg}^{-1}$) and certain molecular mass (about 1000–4000) polyester polyols in the further stage usually with a metal catalyst and low vacuum. Thus we investigate the influence of residence time, monomer feed ratio and reaction pressure on the BRDT reactor performance using the model according to above reaction temperature distribution.

4.2.1 Effect of residence time

Figure 8 shows the effect of residence time on the conversion of AA. As the residence time increases, the E_s of the esterification products at the BRDT bottom increases, while the effect is not significant for long residence time (more than 20 min) due to the chemical and phase equilibria.

4.2.2 Effect of feed ratio

The monomer feed ratio is an important operating

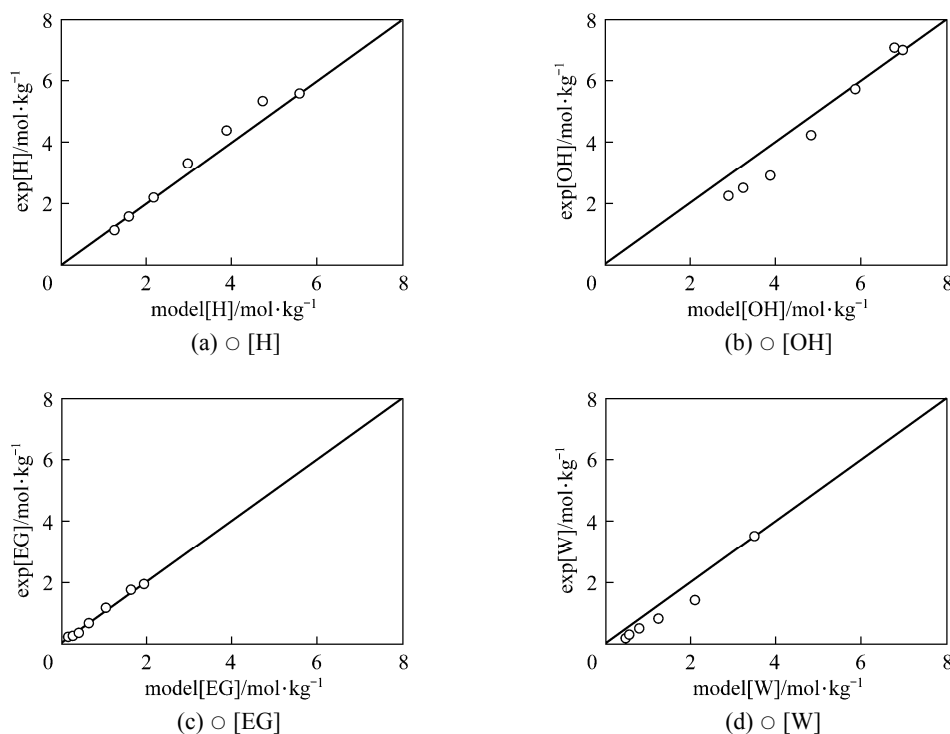


Figure 7 Comparison of experimental and simulation results (feed ratio of EG to AA: 1.2; pressure: 101.325 kPa; residence time on each column tray: 15 min)

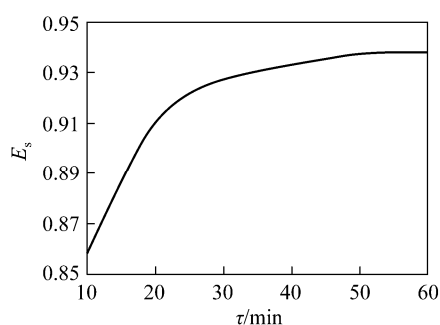


Figure 8 Effect of residence time on E_s of esterification products (feed ratio of EG to AA: 1.2; pressure: 101.325 kPa)

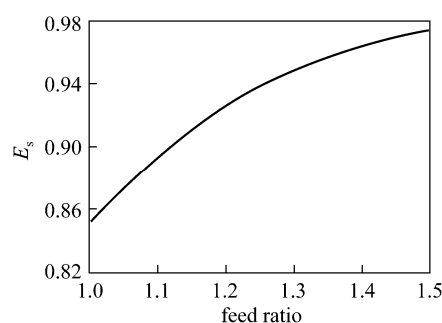


Figure 9 Effect of feed ratio on E_s of esterification products (pressure: 101.325 kPa; residence time on each tray: 30 min)

variable in esterification process. Generally EG is in excess compared to AA, so more EG is available to increase the conversion of AA, see Fig. 9. The increase of E_s is slower with the increase of feed ratio due to the chemical and phase equilibria. Moreover, esterification products will be polymerized to polyester polyol products with low acid value and molecular mass about 1000–4000 in the further stages with low vacuum. Thus the difference between [OH] and [H] of the esterification products must be between 1–3 $\text{mol} \cdot \text{kg}^{-1}$. Fig. 10 shows the effect of feed ratio on the difference between [OH] and [H] of the esterification products. The suitable feed ratio is between 1.1–1.3.

4.2.3 Effect of reaction pressure

Esterification reactions for polyester polyols are

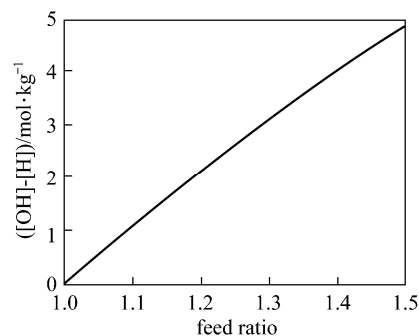


Figure 10 Effect of feed ratio on the difference between [OH] and [H] of esterification products (pressure: 101.325 kPa; residence time on each tray: 30 min)

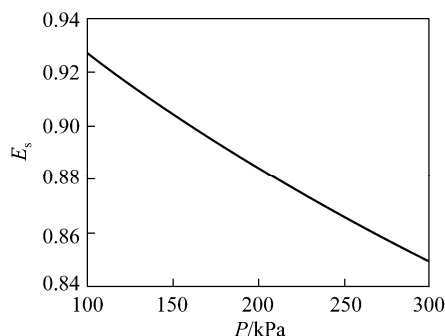


Figure 11 Effect of pressure on E_s of esterification products (feed ratio of EG to AA: 1.2; residence time on each tray: 30 min)

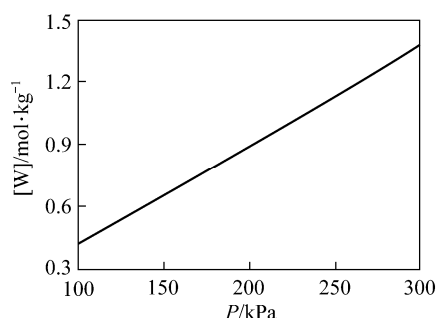


Figure 12 Effect of pressure on water concentration of esterification products (feed ratio of EG to AA: 1.2; residence time on each tray: 30 min)

reversible. The esterification stage is generally operated under atmospheric pressure. In Figs. 11 and 12, E_s decreases as pressure increases, because the water concentration in reactant liquid phase is increased at higher pressures.

5 CONCLUSIONS

A bubbling reactive distillation tower was invented for continuous esterification of polyester polyols. In this new type of reactor, direct esterification between ethylene glycol and adipic acid was accomplished efficiently and rapidly in a counter-current column reactor operated continuously at atmospheric pressure. Based on the kinetic and thermodynamic equations, a comprehensive mathematical model for the continuous esterification process was developed. The influence of the major operating conditions, such as residence time, monomer feed ratio and reaction pressure, on reactor performance was simulated. Simulation results were in good agreement with experimental data, providing strategies for developing and optimizing this process.

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