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Modeling, simulation and analysis of the liquid-phase catalytic oxidation of toluene

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ABSTRACT

The liquid-phase, catalytic oxidation of toluene with air in a continuous stirred tank reactor has become the main technology for producing benzoic acid. Designs are aimed at obtaining high product conversion rates but the reaction is strongly exothermic and therefore it is also important to maintain stable operation to guarantee product quality. However, there is currently no suitable process simulation model available for study. In this paper, a mathematical model of the reaction system is established and validated by comparison to literature data. Steady-state variables were calculated for a series of the operating conditions, using the homotopy continuation method, revealing the existence of multiple steady-state solutions. Two steady-state solutions were found for each operating condition, which had different conversion rates and sensitivities to changes in operating conditions. The operating point having the highest conversion rate was the most sensitive to changes in operating conditions, thus requiring a superior control system. A trade off must be carried out between conversion rate and production stability. Consequently, in practice, a number of factors must be considered simultaneously to select a compromise design.

1. Introduction

Benzoic acid is an important chemical product that is widely used in the production of pharmaceuticals, dye intermediates, plasticizers, spices and food preservatives. The global consumption of benzoic acid recently exceeded 800,000 tons per annum.

There are three main methods for producing benzoic acid: liquid-phase oxidation of toluene with air [1–4], hydrolysis of trichlorobenzylidene [3] and decarboxylation of phthalic anhydride [3]. Of these methods, the liquid-phase oxidation of toluene with air in a continuous stirred tank reactor has become the main technology for producing benzoic acid. The process is strongly exothermic and therefore it is important to maintain stable operation to guarantee product quality. For example, if the heat of reaction is not removed quickly enough, the operation may become unstable and cause an accident. At the same time, the reaction is strongly nonlinear, a situation known to lead to multiple steady-state solutions [5] that has attracted much attention. Uppal et al. [6] studied the dynamic behavior of continuous stirred tank reactors. Balakotaiah and Luss [7] and Qi-peng and Zhongming [8] used bifurcation theory for the multiple steady-state solutions of reactors. Razon and Schmitz [9] reviewed multiple states and instabilities in chemical reaction systems, citing more than 400 articles, and pointed out that reaction systems may have oscillatory characteristics [10]. Seider [11,12] also studied multiple steady-state solutions for reactors, some of which are unstable. One of the main algorithms used in nonlinear analysis is the homotopy continuation method [13–18].

In the first section of this paper, the toluene oxidation process is studied in depth, based on previous research results. In the second section, the chemical reaction in a continuous stirred tank reactor is described and the reaction system model is then established for simulation of the reactor in the third section, using literature and thermodynamic data. The simulated result is shown to be valid by comparison with the literature. In the fourth section, the multiple steady states and their sensitivities to various operating conditions are studied. After analysis of the results, two conclusions can be drawn: the current operating point does not have the highest conversion rate, so the operating conditions could be altered to achieve a higher conversion rate; and a trade off between the conversion rate and production stability (stable product concentration) is necessary when deciding on the operating conditions. Conclusions are given in the last section.

2. Chemical reaction

The main reaction in the process is the reaction of toluene with oxygen on a catalyst [3] to generate benzoic acid and water, giving off reaction heat, the reaction is shown in Fig. 1.

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Nomenclature

A	heat transfer area (m^2)
C_i	reactant or product concentration ($mol\,m^{-3}$)
Cp_m	average heat capacity of mixture ($J\,kg^{-1}\,K^{-1}$)
CP_c	heat capacity of cooling water ($J\,kg^{-1}\,K^{-1}$)
C_{i0}	the initial concentration of ith substance ($mol\,m^{-3}$)
Cp_i	heat capacity of substances i ($J\,mol^{-1}\,K^{-1}$)
E_i	activation energy of reaction i ($kJ\,mol^{-1}$)
k_{0i}	reaction rate constant
M_i	molecular weight of substance i ($g\,mol^{-1}$)
n_{ij}	reaction order in ith reaction for substance j
Q	flow rate of feed flow ($m^3\,s^{-1}$)
Q_c	flow rate of cooling water ($m^3\,s^{-1}$)
R_i	reaction rate ($mol\,m^3\,s^{-1}$)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
T	temperature of reactor (K)
T_c	temperature of cooling jacket (K)
T_f	temperature of feed flow (K)
T_{cf}	temperature of cooling water (K)
U	heat transfer coefficient ($J\,m^{-2}\,s^{-1}\,K^{-1}$)
V	reactor volume (m^3)
V_c	volume of cooling jacket (m^3)

Greek letters

ΔH_r	total reaction heat ($J\,s^{-1}$)
ΔH_x	removed heat ($J\,s^{-1}$)
γ	unit convert coefficient
ρ	density of mixture ($kg\,m^{-3}$)
ρ_c	density of cooling water ($kg\,m^{-3}$)
ΔH_i	reaction heat of the ith reaction ($J\,mol^{-1}$)

Liquid-phase catalytic oxidation of toluene with air has become the main technology for producing benzoic acid, in practice, the reaction takes place in a continuously stirred tank reactor, with a flow sheet as shown in Fig. 2.

Benzyl alcohol, benzoic acid and benzyl benzoate are the primary products in the process of toluene oxidation. The full set of reactions that take place in the reactor are more complex than shown in Fig. 1, as listed below in Fig. 3.

3. Mathematic model

According to data in the literature [1,19], combined with thermodynamic data, the mathematical model for the toluene liquid-phase catalytic oxidation reaction system consists of three parts: the kinetic model, the thermodynamic data and the ordinary differential equations that describe the material balance and energy balance.

The first part is the kinetic model of reactions that take place in reactor, the model is proposed to simulate an industrial toluene oxidation process and the parameters are obtained by nonlinear regressions with industrial data [19]. The kinetic model in this part is fundamental of the material balance in reactions model.

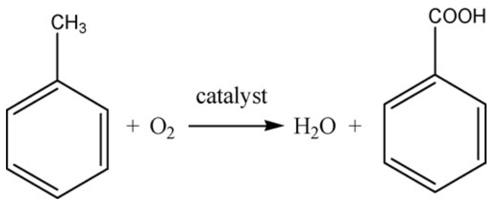

Fig. 1. The toluene oxidation reaction.

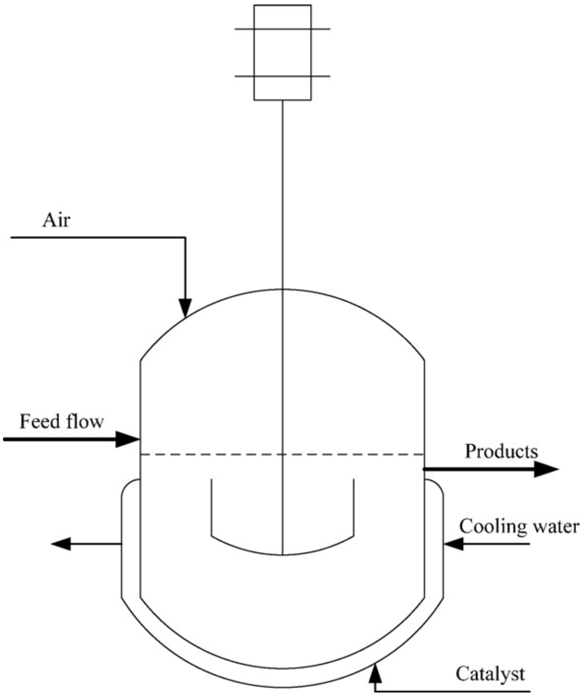

Fig. 2. Flow sheet of a continuous stirred tank reactor for the oxidation of toluene with air.

$$k_{01} = e^{7.5665}$$
$$k_{02} = e^{9.1639}$$
$$k_{03} = e^{-2.1241}$$
$$k_{04} = e^{12.2069}$$
$$k_{05} = e^{17.2712}$$
$$R = 8.314$$
$$E_1 = 5889.878R$$
$$E_2 = 5378.419R$$
$$E_3 = 2200.704R$$
$$E_4 = 6201.636R$$
$$E_5 = 10,020.724R$$
$$n_{11} = 1.0$$
$$n_{12} = 1.88$$
$$n_{21} = 0.88$$
$$n_{22} = 1.35$$
$$n_{31} = 1.15$$
$$n_{32} = 1.39$$
$$n_{41} = 1.075$$
$$n_{51} = 1.36$$
$$n_{52} = 1.5$$
$$\gamma = \frac{1000}{60}$$
$$R_1 = k_{01} e^{-E_1/RT} \left(\frac{C_1}{1000}\right)^{n_{11}} \left(\frac{C_2}{1000} + \frac{C_3}{1000}\right)^{n_{12}} \gamma$$
$$R_2 = k_{02} e^{-E_2/RT} \left(\frac{C_1}{1000}\right)^{n_{21}} \left(\frac{C_2}{1000}\right)^{n_{22}} \gamma$$
$$R_3 = k_{03} e^{-E_3/RT} \left(\frac{C_1}{1000}\right)^{n_{31}} \left(\frac{C_2}{1000} + \frac{C_3}{1000}\right)^{n_{32}} \gamma$$
$$R_4 = k_{04} e^{-E_4/RT} \left(\frac{C_2}{1000}\right)^{n_{41}} \gamma$$
$$R_5 = k_{05} e^{-E_5/RT} \left(\frac{C_3}{1000}\right)^{n_{51}} \left(\frac{C_4}{1000}\right)^{n_{52}} \gamma$$

The second part is the thermodynamic data, the reaction heat and substances heat capacity are regressed by data from reference book, and the data in this part is fundamental of the energy balance

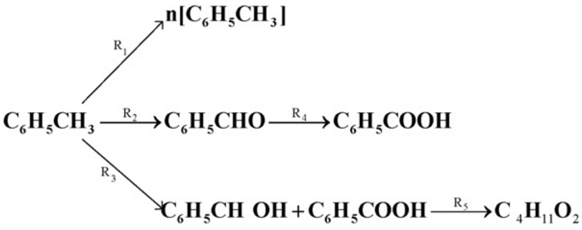

Fig. 3. Reactions occurring in the reactor.

in reaction model.

$$\Delta H_1 = \Delta H_5$$
$$\Delta H_2 = 1000(0.1206T - 516.1)$$
$$\Delta H_3 = 1000(0.0503T - 271.25)$$
$$\Delta H_4 = 1000(-0.0129T - 250.49)$$
$$\Delta H_5 = 1000(0.0759T - 111.32)$$
$$Cp_1 = 0.3531T + 49.169$$
$$Cp_2 = -0.0002T^2 + 0.4267T + 0.517$$
$$Cp_3 = -0.0002T^2 + 0.511T - 21.954$$
$$Cp_4 = -0.0002T^2 + 0.4823T - 22.701$$
$$Cp_5 = -0.0004T^2 + 0.9168T - 47.819$$
$$Cp_6 = Cp_1$$
$$M_1 = 92$$
$$M_2 = 106$$
$$M_3 = 108$$
$$M_4 = 122$$
$$M_5 = 212$$
$$M_6 = 92$$
$$Cp_m = \frac{Cp_1C_1 + Cp_2C_2 + Cp_3C_3 + Cp_4C_4 + Cp_5C_5 + Cp_6C_6}{C_1M_1 + C_2M_2 + C_3M_3 + C_4M_4 + C_5M_5 + C_6M_6} \times 1000$$
$$\rho = 867$$
$$\rho_c = 1000$$
$$Cp_c = 4.183 \times 1000$$
$$\Delta H_r = -V(R_1\Delta H_1 + R_2\Delta H_2 + R_3\Delta H_3 + R_4\Delta H_4 + R_5\Delta H_5)$$
$$\Delta H_x = UA\frac{T + T_f - T_c - T_{cf}}{2}$$

The third part is the ordinary differential equations that describe the dynamic characteristic of material balance and energy balance. The reactor is treated as an ideal continuous stirred tank reactor.

$$\frac{dC_1}{dt} = \frac{Q}{V}(C_{10} - C_1) - (R_1 + R_2 + R_3)$$
$$\frac{dC_2}{dt} = \frac{Q}{V}(C_{20} - C_2) + R_2 - R_4$$
$$\frac{dC_3}{dt} = \frac{Q}{V}(C_{30} - C_3) + R_3 - R_5$$
$$\frac{dC_4}{dt} = \frac{Q}{V}(C_{40} - C_4) + R_4 - R_5$$
$$\frac{dC_5}{dt} = \frac{Q}{V}(C_{50} - C_5) + R_5$$
$$\frac{dC_6}{dt} = \frac{Q}{V}(C_{60} - C_6) + R_1$$
$$\frac{dT}{dt} = \frac{Q}{V}(T_f - T) + \frac{\Delta H_r - \Delta H_x}{\rho Cp_m V}$$
$$\frac{dT_c}{dt} = \frac{Q_c}{V_c}(T_{cf} - T_c) + \frac{\Delta H_x}{\rho_c Cp_c V_c}$$

In the model, it is assumed that biphenyl and benzene have similar physical properties. The biphenyl mass fraction is expected to be less than 1.5% [19], so this assumption is reasonable for this reaction system.

Table 1
Initial values of reaction system state variables.

Parameter	Value	Units
C_1	6803.703	mol/m^3
C_2	197.547	mol/m^3
C_2	197.547	mol/m^3
C_3	73.172	mol/m^3
C_4	2541.710	mol/m^3
C_5	45.120	mol/m^3
C_6	169.402	mol/m^3
T	439	K
T_c	290	K

Table 2
Values of reaction system parameters.

Parameter	Value	Units
Q_c	1.6	m^3/s
T_f	298	K
T_{cf}	285	K
UA	880,452.5	W/K
V	236	m^3
V_c	100	m^3

Thermodynamic model equations are available within the temperature range of interest. The heat of reaction (kJ/mol) equation is valid from 273.15 to 1173.15 K and the heat capacity (J/(mol K)) equation is valid from 273.15 to 1273.15 K. The results from the following calculation are located within these temperature ranges.

The initial values of state variables for the model are shown in Table 1.
The parameters of the model are shown in Table 2.

The simulated mass fraction results are listed in Table 3, from which it can be seen that the simulated results are quite close to the literature data. The simulated temperature was 166.3 °C, which is very close to the 166 °C reported in the literature [19].

4. Nonlinear analysis

The liquid-phase oxidation of toluene with air is a strongly nonlinear reaction system so it is useful to analyze the nonlinear characteristics of the system during both process design and operation control. Usually, it is difficult to solve nonlinear systems. Here, the homotopy continuation method [13–18] is used because, in some cases, it is the only method that can find the solution for nonlinear systems. Also, this method is a powerful tool for solving problems involving a series of operating variable values. In this reaction system, the feed flow rate could vary, due to uncertain factors, so it is useful to solve the system for variable feed flow rates.

Figs. 4 and 5 show the product concentrations and reactor temperatures with changes to the feed flow rate. Fig. 6 shows the product concentrations with changes to the temperature.

From Figs. 4 and 5, it can be seen that the system has two steady-state operating points at each feed flow rate. Fig. 6 shows that there

Table 3
Simulation results.

Item	Simulation result	Industrial data	Error (%)
Toluene mass fraction	0.6261	0.6320	−0.9
Benzaldehyde mass fraction	0.0216	0.0203	6.3
Benzyl alcohol mass fraction	0.0082	0.0084	−2.8
Benzoic acid mass fraction	0.3194	0.3261	−2.1

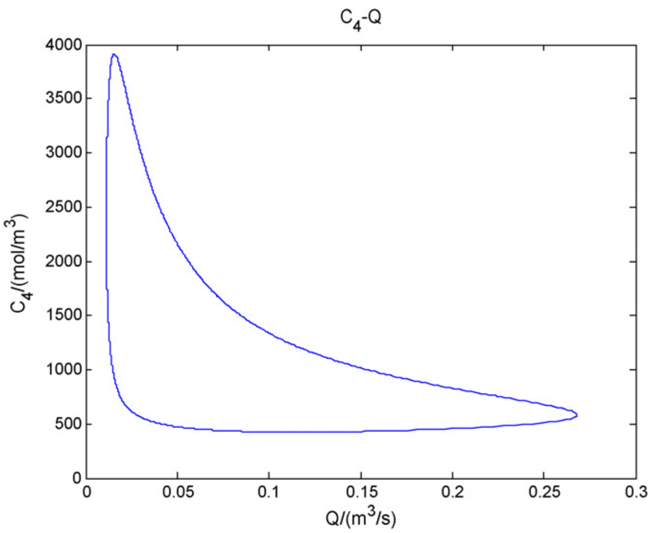

Fig. 4. Product concentration changes with flow rate.

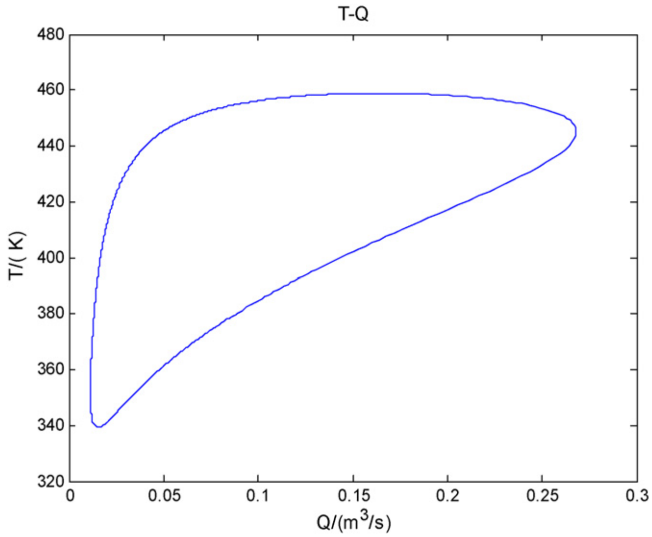

Fig. 5. Temperature changes with flow rate.

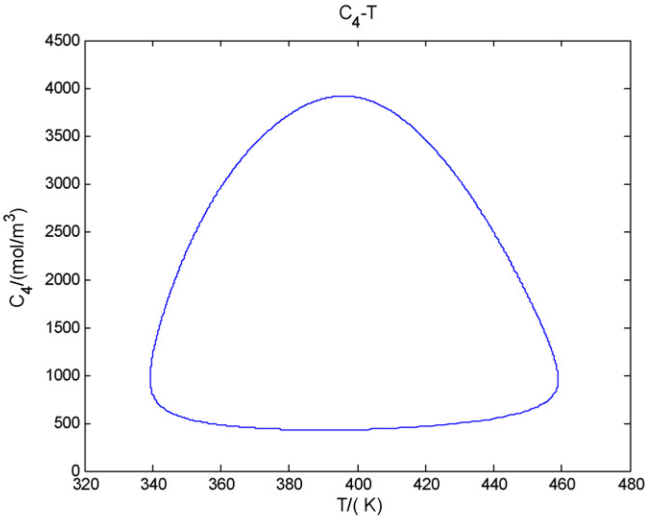

Fig. 6. Product concentration changes with temperature.

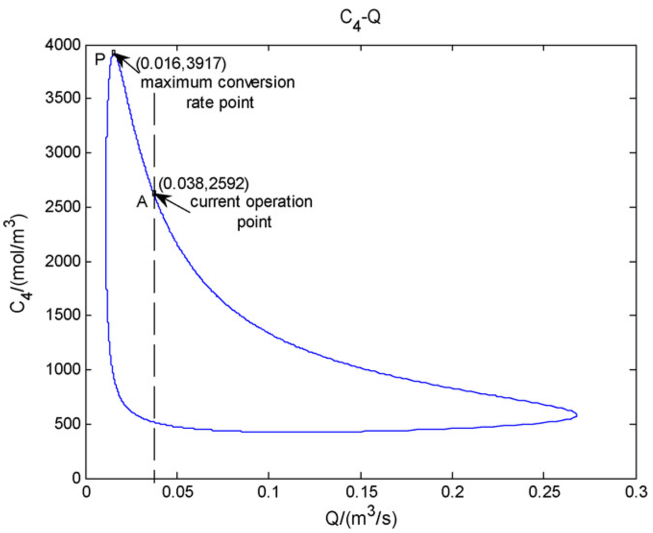

Fig. 7. Current operation point and the highest conversion point.

are also two steady-state operating points at a certain temperature. Fig. 7 shows the current operating point A and the point P with the highest conversion rate. Thus, according to the conversion rate, a better operating point exists. However, it was found through this analysis that the point with the highest conversion rate is not easy to maintain in terms of production stability, which provides important guidance for plant operation. The situation is described in Fig. 8.

Fig. 8 shows different operating points, such as points A–D, with different characteristics in conversion rate and production stability. Under equal changes from A to B and from C to D, the production conversion rate changes differ significantly. In practice, this means that the production stability differs from point to point when the feed flow rate changes. Point A has higher conversion but lower production stability, while point D has a lower conversion rate and higher production stability. Therefore, if point A is chosen as the operating point, a better control system is required. Because the conversion rate and the production stability conflict with each other, a number of factors must be considered simultaneously in practice to select a compromise design.

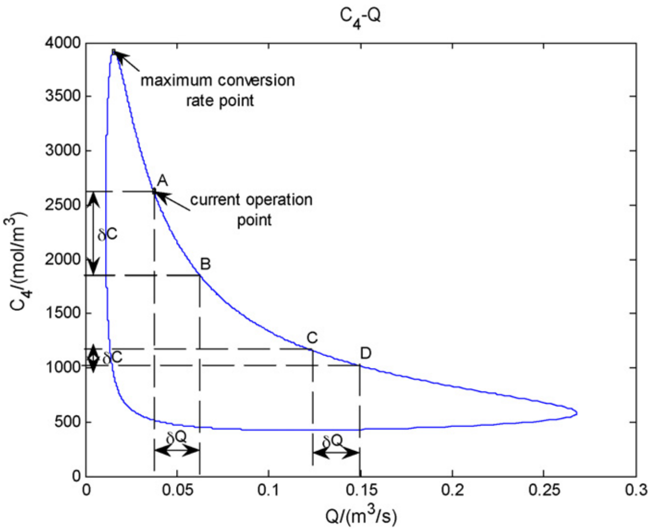

Fig. 8. Different results when flow rate changes occur.

5. Conclusions

Currently, the liquid-phase, catalytic oxidation of toluene with air has become the main technology for producing benzoic acid. In this paper, a mathematic model was established and validated by comparing the simulation results with literature data. The steady-state variables (the product concentration and the reactor temperature) of the system were obtained under different operating conditions, using the homotopy continuation method. The results show that there are multiply steady states in the system and there are upper and lower constraints to the feed flow rate. The system characteristics varied within the constrained feed flow rate range.

Observation over a wide range of operating points (Fig. 8), showed that the current operating point did not produce the highest conversion rate and that the product concentration at this point was sensitive to changes in the feed flow rate, meaning that production stability was poor. Although the operating point with the highest conversion rate was identified, the production stability at that point was also poor. In Fig. 8, it can be seen that when flow rate was low the conversion rate was high but the production stability was low and when the flow rate was higher the conversion rate was lower but the production stability was improved. Therefore, the conversion rate and the production stability conflict with each other. Consequently, in practice, a number of factors must be considered simultaneously to select a compromise design.

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