

Simulation and Optimization in the Process of Toluene Liquid-phase Catalytic Oxidation

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Abstract Liquid-phase oxidation of toluene with air has become the main technology for producing benzoic acid in a reactor at present. Based on the kinetic model of the toluene oxidation process obtained from laboratory and mass balance of key component, a novel model is established to simulate the industrial toluene oxidation process, in which the effects of benzaldehyde and benzyl alcohol are considered and the kinetic parameters are revised by industrial data. The simulation results show that the error of benzoic acid yield is within 3.5%. Based on the simulation model, to maximize the benzoic acid yield, an optimization model is proposed to optimize the operating parameters, including toluene feed-in mass flux and temperature. The optimization result indicates that on the allowable operating conditions, the maximum benzoic acid yield obtained with the reaction temperature at 167.2°C and the mass flux at 104.1 t·h⁻¹ is greater than the current one, which can be used to guide industrial reactor's operation.

Keywords toluene, benzoic acid, catalytic oxidation, simulation, optimization

1 INTRODUCTION

Benzoic acid is an important raw material to produce phenol and caprolactam. At present, liquid-phase oxidation of toluene with air has become the main technology for producing benzoic acid in the industry [1, 2]. Nevertheless, the reactive process is strongly exothermic and explosive. The simulation and optimization in the process of toluene liquid-phase catalytic oxidation can guide the industrial reactor's operations, so as to ensure the operation safety and the product quality.

According to the kinetic equations proposed by Bhattacharya *et al.* [3], Yu [4] established a dynamic simulation model for the process of toluene oxidation, and used it to investigate the rules on how the reaction results are influenced by reaction temperature, toluene/air ratio, and toluene feed-in mass flux. Tang [5] studied the kinetics of the toluene oxidation process in a bubble column reactor under conditions close to the industrial parameters. Based on the experimental results, Tang proposed another kinetic model and applied it to simulate an industrial reactor. However, both kinetic models used by Yu and Tang have neglected the effects of benzaldehyde and benzyl alcohol which are important to the reaction [6–10]. The experimental conditions are significantly distinguishable from the industrial conditions; therefore, the kinetic parameters obtained from the experimental results need to be adjusted.

Based on the kinetic model of the toluene oxidation process obtained from laboratory and mass balance of key component, this article proposed a new model to simulate the industrial toluene oxidation process, which considered the effects of benzaldehyde and benzyl alcohol [11–17]. The parameters of the model are obtained by nonlinear regressions with industrial data, so as to accurately calculate the benzoic acid concentration and yield. Based on the simulation

model, to maximize the benzoic acid yield, an optimization model is developed to optimize the operating parameters, including the toluene feed-in mass flux and temperature.

2 MATHEMATICAL FORMULATION

2.1 Kinetic model

Benzyl alcohol, benzoic acid, and benzyl benzoate are the primary products in the process of toluene oxidation. Fig. 1 shows the reactive paths in the process of toluene liquid-phase catalytic oxidation.

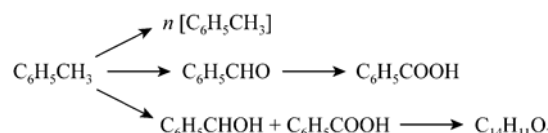


Figure 1 Reactive paths in the process of toluene liquid-phase catalytic oxidation

The major factors that influence the rate of toluene oxidation reaction are the reactant concentrations and the reaction temperature [18, 19]. The reaction rates can be written as Eqs. (1)–(4):

$$-\frac{dc_1}{dt} = k_{01}e^{-\frac{E_1}{RT}}c_1^{n11}(c_2 + c_3)^{n12} + k_{02}e^{-\frac{E_2}{RT}}c_1^{n21}c_2^{n22} + k_{03}e^{-\frac{E_3}{RT}}c_1^{n31}(c_2 + c_3)^{n32} \quad (1)$$

$$\frac{dc_2}{dt} = k_{02}e^{-\frac{E_2}{RT}}c_1^{n21}c_2^{n22} - k_{04}e^{-\frac{E_4}{RT}}c_2^{n41} \quad (2)$$

$$\frac{dc_3}{dt} = k_{03}e^{-\frac{E_3}{RT}}c_1^{n31}(c_2 + c_3)^{n32} - k_{05}e^{-\frac{E_5}{RT}}c_3^{n51}c_4^{n52} \quad (3)$$

$$\frac{dc_4}{dt} = k_{04} e^{-\frac{E_4}{RT}} c_2^{n_{41}} - k_{05} e^{-\frac{E_5}{RT}} c_3^{n_{51}} c_4^{n_{52}} \quad (4)$$

There are 19 kinetic parameters in Eqs. (1)–(4), which can be divided into three categories:

- (1) Pre-exponential factors: $k_{01}, k_{02}, k_{03}, k_{04}, k_{05}$;
- (2) Energy of activation: E_1, E_2, E_3, E_4, E_5 ;
- (3) Reaction order: $n_{11}, n_{12}, n_{21}, n_{22}, n_{31}, n_{32}, n_{41}, n_{51}, n_{52}$.

2.2 Simulation method

The industrial reactor is a continuous stirred-tank. The material balance for the key components can be written as Eq. (5):

$$v_0(c_i - c_{i0}) = V \frac{dc_i}{dt} \quad (i = 1, 2, 3, 4) \quad (5)$$

The concentrations of the four key components can be obtained when solving the model consisting of Eqs. (1)–(5) by Newton's method.

2.3 Regression of kinetic parameters

The pre-exponential factors and the energy of activation are usually thought to be constants. However, the reaction order can change with the reaction conditions such as temperature, pressure, concentrations, and properties of the solvent. To simulate the industrial reaction process better, the kinetic parameters, especially the reaction order, which are obtained from laboratory experimental results, must be adjusted.

Let $\mathbf{x} = (T, v_0)^T$ and $\boldsymbol{\beta} = (n_{11}, n_{12}, n_{21}, n_{22}, n_{31}, n_{32}, n_{41}, n_{51}, n_{52})^T$; $\mathbf{x}$ is a vector of independent variable and $\boldsymbol{\beta}$ is a vector of regression coefficient. By simulating the toluene oxidation process, the benzoic acid mass fraction y can be calculated using $\mathbf{x}$ and $\boldsymbol{\beta}$, as shown in Eq. (6):

$$y = f(\mathbf{x}, \boldsymbol{\beta}) \quad (6)$$

The industrial data is then used to form a nonlinear optimization problem without constraints, as shown in Eq. (7)

$$\min S = \sum_{i=1}^n [f(\mathbf{x}_i, \boldsymbol{\beta}) - y_i^0]^2 \quad (7)$$

Hooke-Jeeves algorithm is effective to solve the problem. A new group of reaction orders can be obtained after solving the regression problem:

$$\boldsymbol{\beta}^* = (n_{11}^*, n_{12}^*, n_{21}^*, n_{22}^*, n_{31}^*, n_{32}^*, n_{41}^*, n_{51}^*, n_{52}^*)^T$$

2.4 Optimization model

To ascertain the optimal operating conditions and the maximum benzoic acid yield, an optimization problem [20] of the toluene oxidation process is formulated as Eqs. (8)–(12):

$$\max Y = v \cdot \eta \cdot y \quad (8)$$

$$\text{s.t. } T_{\min} \leq T \leq T_{\max} \quad (9)$$

$$v_{\min} \leq v \leq v_{\max} \quad (10)$$

$$y \geq y_{\min} \quad (11)$$

$$y = f(\mathbf{x}, \boldsymbol{\beta}) \quad (12)$$

The constraints (9) and (10) show the allowable operating conditions.

3 RESULTS AND DISCUSSIONS

3.1 Simulation results and discussion

Table 1 presents the simulation results when the reaction temperature is 166°C, the toluene feed-in mass flux is 102.6 t·h⁻¹, and $\eta = 0.3571$. The results show that both the errors of benzoic acid yield and benzoic acid concentration are within 3.5%.

Table 1 Simulation results

Item	Industrial data	Simulation result	Error/%
toluene mass fraction	63.2%	59.6960%	5.54
benzaldehyde mass fraction	2.03%	2.1081%	3.85
benzyl alcohol mass fraction	0.84%	0.9162%	9.07
benzoic acid mass fraction	32.61%	33.7458%	3.48
toluene conversion	10%	10.0014%	0.014
benzoic acid yield	12 t·h ⁻¹	12.3654 t·h ⁻¹	3.05

3.2 Optimization results and discussion

For the actual industrial process, in a reaction temperature ranging from 164.8°C to 167.2°C and a toluene feed-in mass flux ranging from 79.7 t·h⁻¹ to 104.1 t·h⁻¹, the maximum benzoic acid yield is 12.57 t·h⁻¹, which can be obtained when the reaction temperature is 167.2°C and the mass flux is 104.1 t·h⁻¹. The current benzoic acid yield is 12.3654 t·h⁻¹, when the reaction temperature is 166°C and mass flux is 102.6 t·h⁻¹; thus, it still has a possible enhancement

4 CONCLUSIONS

According to the kinetic model obtained from laboratory and the material balance for the four key components, a novel model is established to simulate the industrial toluene oxidation process. The simulation results show that the error of benzoic acid yield is within 3.5%. To maximize the benzoic acid yield, an optimization model is proposed to optimize the operating parameters, including the toluene feed-in mass flux and temperature. The optimization result shows that on the allowable operating conditions, the maximum benzoic acid yield obtained when the reaction temperature is 167.2°C and mass flux is 104.1 t·h⁻¹ is greater than the current one. The optimization results can be used to guide industrial reactors' operations.

NOMENCLATURE

c_1	toluene concentration, $\text{mol}\cdot\text{L}^{-1}$
c_2	benzaldehyde concentration, $\text{mol}\cdot\text{L}^{-1}$
c_3	benzyl alcohol concentration, $\text{mol}\cdot\text{L}^{-1}$
c_4	benzoic acid concentration, $\text{mol}\cdot\text{L}^{-1}$
T	reaction temperature, K
V	effective volume of the reactor, L
v	toluene feed-in mass flux, $\text{t}\cdot\text{h}^{-1}$
v_0	toluene feed-in volume flux, $\text{L}\cdot\text{min}^{-1}$
Y	maximum benzoic acid yield, $\text{t}\cdot\text{h}^{-1}$
y	benzoic acid mass fraction
y^0	actual benzoic acid mass fraction
η	liquid output mass flux/toluene feed-in mass flux

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