



Estimation of kinetic parameters for the reactor model of the phthalic anhydride production by the design of experiments



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ARTICLE INFO

Article history:

Received 14 June 2014

Received in revised form 3 September 2014

Accepted 7 September 2014

Available online 16 September 2014

Keywords:

Kinetic parameters

Reactor model

o-Xylene

Phthalic anhydride

Design of experiments

ABSTRACT

Heterogeneous reactor model was developed to predict product, by-product and hot spot temperature in an industrial fixed bed reactor of phthalic anhydride production. This work modified the Calderbank's kinetic model by including the reaction from *o*-xylene to by-product maleic anhydride. The kinetic parameters appropriating to the catalyst in this study were estimated by the design of experiments. The reactor model was validated by comparing the simulated results with the production data in terms of the outlet molar flow rates of phthalic anhydride and maleic anhydride, and the hot spot temperature. The results were less than 1.8% deviated.

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Introduction

Phthalic anhydride (PA) is extensively used in the production of various chemicals such as polyester resin [1,2]. It is produced commercially by partial oxidation of *o*-xylene (OX) over V₂O₅/TiO₂ catalyst in a multi-tubular fixed bed reactor at 300–450 °C. The reaction can be achieved at a conversion greater than 99% and 77% selectivity. The main products consist of PA, *o*-tolualdehyde (OT), phthalide (PL) and carbon oxides (CO_x). However, by-products such as maleic anhydride (MA), *o*-toluic acid and benzoic acid at low concentrations are inevitable [3–5].

Although a number of kinetic studies on the OX partial oxidation were available, the reaction network of the OX partial oxidation is still not accomplished since the experimental conditions including details of the catalysts from those studies were different [3]. So far, the reaction networks of the OX partial oxidation to PA are mostly referred to either the redox-based kinetic model by Calderbank et al., or the kinetic model proposed by Skrzypek et al. which is based on adsorption mechanism and more complicate [2,6–11]. Mongkhonsri [12] and Anastasov [13,14], for example, used the Calderbank's kinetic model to

predict the amounts of products and by-products, hot spot temperature in the V₂O₅/TiO₂ catalyst bed, and the catalyst activity.

As a matter of fact, the kinetic parameters (i.e., pre-exponential factors and activation energies of each reaction in the reaction network of the kinetic model) indicate how the reactions go on and relate to the product yield and temperature profile of the reaction. The kinetic parameters depend on catalyst characteristics and are typically obtained from the experiments in a laboratory scale. Such experiments for OX partial oxidation study require high cost equipment for a safe system as the reaction is highly exothermic with heat of reaction of 1.285 MJ/mol [6]. Basically, a suitable mathematical reactor model is an alternative to obtain the required industrial operating parameters at the minimum cost. Authayanun et al. [15] developed a pseudo-homogeneous model of an industrial fixed bed reactor for catalytic hydrogenation of pyrolysis gasoline, and estimated the reaction kinetic parameters. Anastasov [13] used a two-dimensional heterogeneous model to estimate the kinetic parameters for the OX partial oxidation in the fixed bed reactor. Prediction from the model in terms of the amounts of PA and PL, and the temperature profile along the catalyst bed agreed well with the plant data.

In this paper, we developed two-dimensional heterogeneous model for high accuracy prediction of the amounts of PA and MA, and the hot spot temperature in an industrial multi-tubular fixed bed reactor by including the reaction pathway from OX to a

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Nomenclature

a	specific external surface area of catalyst pellet (m^2/m^3)
A_i	pre-exponential factors of the i^{th} reaction step ($\text{kmol}/\text{kg s Pa}$)
C_i	concentration of i component in gas phase (mol/m^3)
C_{pi}	concentration of i component on the catalyst surface (mol/m^3)
C_C	specific heat capacity of coolant ($\text{J}/\text{m}^3 \text{K}$)
C_P	specific heat capacity of gas phase ($\text{J}/\text{m}^3 \text{K}$)
$C_{i,0}$	inlet concentration of i component in gas phase (mol/m^3)
d_p	diameter of catalyst pellet (m)
D_m	gas diffusivity (m^2/s)
D_r	effective gas diffusivity in radial direction (m^2/s)
E_i	activation energy of the i^{th} reaction step (kJ/kmol)
h_{gc}	heat transfer coefficient between gas phase and coolant ($\text{W}/\text{m}^2 \text{K}$)
h_{gp}	heat transfer coefficient between gas phase and catalyst pellet ($\text{W}/\text{m}^2 \text{K}$)
h_{gw}	heat transfer coefficient between gas phase and reactor tube wall ($\text{W}/\text{m}^2 \text{K}$)
ΔH_{rxn}	heat of the reaction (kJ/kmol)
k_g	thermal conductivity of gas phase ($\text{W}/\text{m K}$)
k_r	effective thermal conductivity of gas phase in radial direction ($\text{W}/\text{m K}$)
k_{gp}	mass transfer coefficient between gas phase and catalyst pellet (m/s)
K_i	reaction rate constant of the i^{th} reaction step ($\text{kmol}/\text{kg s Pa}$)
K_C	reaction rate constant of catalyst re-oxidation ($\text{kmol}/\text{kg s Pa}$)
P_i	partial pressure of i component (Pa)
P_{O_2}	partial pressure of oxygen (Pa)
Pr	Prandtl number
Pr_C	Prandtl number of coolant
r	radial coordinate (m)
$r_{p,i}$	reaction rate on catalyst pellet for the i^{th} step ($\text{kmol}/\text{kg s}$)
R	reactor tube radius (m)
Re	Reynolds number of gas
Re_C	Reynolds number of coolant
Re_e	equivalent Reynolds number = $4V/a\mu$
$R_{p,i}$	reaction rate by i component on catalyst pellet ($\text{kmol}/\text{kg s}$)
Sc	Schmidt number
T	gas temperature (K, °C)
T_c	coolant temperature (K, °C)
T_p	catalyst pellet temperature (K, °C)
T_0	inlet gas temperature (K, °C)
V	superficial gas velocity (m/s)
V_c	coolant velocity (m/s)
z	axial coordinate (m)

Greek symbols

α	defined in Eq. (19), dimensionless
ε	bed porosity

ρ	gas density (kg/m^3)
ρ_b	bulk density of catalyst bed = $\rho_p(1 - \varepsilon)$ where ρ_p is catalyst pellet density (kg/m^3)
μ	gas viscosity (Pa s)

Subscripts

OX	<i>o</i> -xylene
OT	<i>o</i> -tolualdehyde
PL	phthalide
PA	phthalic anhydride
MA	maleic anhydride
i	i component

major-by-product MA in the Calderbank's reaction network. The kinetic parameters were estimated by design of experiments. The significant kinetic parameters were selected by fractional factorial design and readjusted by central composite design (CCD) [16]. The fractional factorial design and the CCD are in the Minitab R. 15 software. The simulated results were validated by comparing with historical production data [17] of the case study PA plant using fresh V_2O_5/TiO_2 catalyst.

Development of the mathematical reactor model

Mass and energy balance equations

Two-dimensional heterogeneous mathematical model suggested by Froment et al. [18] was used to simulate the gas and solid behaviors in the fixed bed reactor. The model is found to be most preferable for the fixed bed reactor [19], especially the reactor operating under highly exothermic condition same as the OX partial oxidation in this work [6]. The assumptions of the model are as follows:

- steady-state operation
- flat inlet gas velocity and temperature profiles
- constant pressure in the reactor
- constant gas physical and transport properties
- mass and heat axial dispersions are neglected due to high gas velocity [20]
- the reactions occur only on the catalyst's external surface due to thin film reactive species on inactive carrier of the V_2O_5/TiO_2 catalyst [21]

The mass and energy balance equations are shown below:
For gas phase:

$$D_r \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - V \frac{\partial C_i}{\partial z} + k_{gp} a (C_{pi} - C_i) = 0 \quad (1)$$

$$k_r \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - V \rho C_P \frac{\partial T}{\partial z} + h_{gp} a (T_p - T) = 0 \quad (2)$$

with boundary conditions:

$$z = 0; \quad C_i = C_{i,0}; \quad T = T_0 \quad (3)$$

$$r = 0; \quad \frac{\partial C_i}{\partial r} = 0; \quad \frac{\partial T}{\partial r} = 0 \quad (4)$$

$$r = R; \quad \frac{\partial C_i}{\partial r} = 0; \quad -k_r \frac{\partial T}{\partial r} = h_{gc} (T - T_c) \quad (5)$$

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