MODELING AND OPTIMIZATION OF A FIXED-BED CATALYTIC REACTOR FOR PARTIAL OXIDATION OF PROPYLENE TO ACROLEIN

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ABSTRACT

This study aims for the optimization of process conditions in a fixed-bed catalytic reactor system with a circulating molten salt bath, in which partial oxidation of propylene to acrolein takes place. Two-dimensional pseudo-homogeneous model is adopted with estimation of suitable parameters and its validity is corroborated by comparing simulation result with experimental data. The temperature of the molten salt and the feed composition are found to exercise significant influence on the yield of acrolein and the magnitude of hot spot. The temperature of the molten salt is usually kept constant. This study, however, suggests that the temperature of the molten salt must be axially adjusted so that the abrupt peak of hot spot should not appear near the reactor entrance. The yield of acrolein is maximized and the position and the magnitude of hot spot are optimized by the method of the iterative dynamic programming (IDP).

INTRODUCTION

The process in a fixed-bed catalytic reactor for the partial oxidation of propylene to acrolein is one of the most important processes in industry. The selectivity of propylene to acrolein is influenced by the process condition and the configuration of reactor system. For this reason, filling a reactor with metal oxide catalyst only may not guarantee a desired optimal selectivity. Therefore, a mathematical model that accurately describes industrial catalytic reactor system is needed to systematically tune the process condition. Then the process condition is optimized by investigating the reactor behavior and finding the best policy.

The catalytic fixed-bed reactor, in which exothermic reaction takes place, usually shows hot spot. If the hot spot can be controlled, a better result may be obtained. So, in this study, the temperature of the molten salt is axially adjusted as operation strategy so that an abruptly high peak in the temperature profile may not appear.

The method of the iterative dynamic programming (IDP) is applied to the fixed-bed catalytic reactor as optimization technique. The IDP is widely used because it is able to find the global optimum for constrained nonlinear system without unduly increasing the dimension of the system or the computational burden.

Much research effort is made to develop mathematical models and optimize the fixed-bed catalytic reactors (Castilla et al., 1988; Zhou et al., 1999). But there are only a few reports on modeling and optimization of the fixed-bed catalytic reactor for partial oxidation of propylene to acrolein. Creten et al. (1995) investigated kinetic model by using temporal analysis of products (TAP) system and applied the kinetic model to simulation study of a commercial process. In addition, Arntz et al. (1982) developed reaction kinetics and obtained effective heat transfer coefficients by experiments for a pilot plant and predicted concentration and reaction temperature quite well with his model.

In this study, firstly, reaction kinetics is investigated and model equations are developed. Then, under various reaction conditions, behavior of the catalytic reactor is examined and validity of the reactor model is corroborated. Finally, optimal process condition is examined by using the method of IDP.

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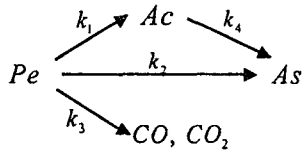
REACTION KINETICS

The following reaction kinetics is proposed for the partial oxidation of propylene to acrolein in fixed-bed catalytic reactor by Arntz(1982)



$$R_1 : Pe + O_2 \xrightarrow{k_1} Ac + H_2O \qquad r_1 = k_1 P_{Pe}^{\ n_{11}} P_{O_2}^{\ n_{12}}$$

$$R_2 : Pe + \frac{3}{2}O_2 \xrightarrow{k_2} As + H_2O \qquad r_2 = k_2 P_{Pe}^{\ n_{21}} P_{O_2}^{\ n_{22}}$$

$$R_3 : Pe + \frac{25}{6}O_2 \xrightarrow{k_3} \frac{2}{3}CO + \frac{7}{3}CO_2 + 3H_2O \qquad r_3 = k_3 P_{Pe}^{\ n_{31}}$$

$$R_4 : Ac + \frac{1}{2}O_2 \xrightarrow{k_4} As \qquad r_4 = k_4 P_{Ac}^{\ n_{43}}$$

where *Pe*, *Ac*, and *As* denote propylene, acrolein, and acrylic acid respectively. *Px* indicates the partial pressure of the component *x*. Byproducts such as acetaldehyde, formaldehyde, acetic acid, etc. are not considered in the mechanism since their quantities produced in the reactor are negligible.

The diameter of spherical catalyst based on a multi-component bismuth molybdate is 0.53cm. Effective kinetic parameters are shown in Table 1, which constitute the following effective reaction rate equation. These parameters were originally reported by Arntz (1982)[3] with a spherical catalyst based on a multi-component bismuth molybdate and some of them are modified to predict the yield of acrolein better.

$$r_{i,eff} = A_i \exp(-\frac{E_i}{RT}) P_{Pe}^{\ n_{i1}} P_{O_2}^{\ n_{i2}} P_{Ac}^{\ n_{i3}}$$

MODELING OF FIXED-BED CATALYTIC REACTOR SYSTEM

One-dimensional pseudo-homogeneous model

This model is based on the following hypotheses:

(1) The concentration and temperature are the same between catalyst particle phase and bulk phase, respectively.

Table 1 Effective kinetic parameters

No.	A_i $mol/m^3 s Pa^{\sum n_{ij}}$	E_i J/mol	n_{i1} (Pe)	n_{i2} (O_2)	n_{i3} (Ac)
1	7.51×10^{-3}	41.8×10^{-6}	0.44	0.93	0
2	1.17	69.8×10^{-6}	0.54	0.54	0
3	4.74	52.8×10^{-6}	0.66	0	0
4	77.1	93.2×10^{-6}	0	0	1