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Periodically operated trickle-bed reactor for EAQs hydrogenation: Experiments and modeling

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Abstract

The influence of periodic operation on a consecutive reaction, the hydrogenation of 2-ethylanthraquinones (EAQs) over Pd/Al_2O_3, on a laboratory-scale trickle-bed reactor (TBR) was studied. The effects of operating parameters including cycle period, split, pressure, temperature, and time-average flow rate on the performance were experimentally examined in comparison with the steady-state operation. The results showed that under the interested operating conditions the conversion and the selectivity improved by 3–21% and 1–12%, respectively. A dynamic model consisting of a set of partial differential equations (PDEs) was developed to simulate the periodic operation of TBR for EAQs hydrogenation. The PDEs were converted into a set of ordinary differential equations (ODEs) using the method of lines (MOL) and then numerically solved by the semi-implicit Runge–Kutta method. The developed model was verified by simulating the effect of cycle period and split on the conversion and the selectivity enhancement and compared with the experimental results. It was found that the model was reliable and satisfactory when the cycle period was less than 200 s.

Keywords: Multiphase reactor; Trickle-bed reactor; Periodic operation; Modeling; Hydrogenation

1. Introduction

The trickle-bed reactor (TBR) is extensively used in hydrotreating and hydrodesulfurization in the refining industry, in hydrogenation, oxidation and hydrodenitrogenation in the petrochemical, biochemical, and water treatment industries (Al-Dahhan et al., 1997; Dudukovic et al., 1999, 2002). Generally TBR has been designed and operated under steady-state mode. However, over the past 10 years the unsteady-state operation mode has generated broad attention and a growing interest because many studies have shown that reactor performance can be improved significantly by periodic modulation of gas or liquid flow rate (Silveston and Hanika, 2002; Boelhouwer et al., 2002).

Haure et al. (1989) firstly proposed the conception of periodic operation of TBR and studied the catalytic SO_2 oxidation over the activated carbon by periodically modulating the water flow between on and off. A significant improvement in SO_2 conversion up to 30–45% was observed, which was explained in terms of steady-state rate with and without water flow for symmetrical and asymmetrical cycles. Haure et al. (1990) set a series of first-order partial differential equations (PDEs) with assumption that feed/drainage were instantaneous to predict the observed traveling thermal fronts. Metzinger et al. (1992, 1994) and Lee et al. (1995) indicated that the controlling resistance of oxygen mass transport could be removed at low split of periodic operation by using activated carbon and Pt-impregnated centaur catalyst. Based on the model of Haure et al. (1990), Stegasov et al. (1994) developed a dynamic heterogeneous mathematic model for the SO_2 oxidation under periodic operation, but in this model the feed/drainage and the axial dispersion behavior were

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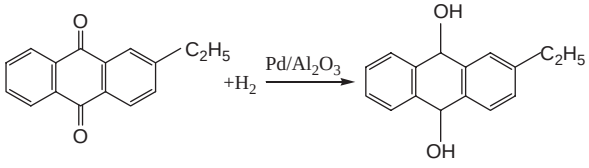
neglected. Lange et al. (1994) investigated the effect of feed composition under PEAK-BASE mode on the temperature variation of the catalyst bed in the hydrogenation of cyclohexene to cyclohexane over Pd/C and the effect of feed flow rate under a ON–OFF mode on the conversion in the hydrogenation of AMS over Pd/alumina catalyst, and observed conversion enhancement of 2–15% for the hydrogenation of AMS. Castellari and Haure (1995), and Gabarain et al. (1997) also studied the hydrogenation of AMS over palladium/alumina catalyst under ON–OFF mode operation and observed 45–400% improvement in conversion over the corresponding steady-state performance. Khadilkar et al. (1999) examined the influence of operating mode on the conversion of AMS hydrogenation for gas and liquid reactant limited reactions by changing operation pressure, and indicated that PEAK–BASE and ON–OFF mode were advantageous for liquid and gas reactant limited reactions, respectively. Turco et al. (2001) further studied the effect of gas and liquid modulation on instantaneous AMS conversion and observed a time-average conversion improvement of 52% for liquid modulation but a negligible effect for gas modulation, which were ascribed to appearance of foams under the transition of trickling to foaming-pulsing regimes. Banchero et al. (2004) confirmed the conclusion of Turco et al. (2001) that the maximum performance could be obtained for periodic operation at the transition of trickling to foaming-pulsing regimes and further indicated that the base time is important for the definition of optimal conditions. Two models were established to predict the conversion enhancement of AMS hydrogenation. Gabarain et al. (1997) developed a one-dimensional pseudo-homogeneous model for AMS hydrogenation, which gave a satisfactory representation of the experimental results, but required the corresponding temperature profile in an operation period to determine time parameters needed for the model. Lange et al. (1999) established a dynamic heterogeneous model and confirmed the possibility of performance enhancement under unsteady-state operation in comparison to steady-state operation. Several other reaction systems including hydrogenation of phenylacetylene (Wilhite et al., 2003), hydrogenation of crotonaldehyde (Stradiotto et al., 1999), wet oxidation of phenol (Tukac et al., 2003), wet oxidation of ethanol (Fraguio et al., 2004), etc., have been reported in the literature. Although a lot of effort has been spent on experimental and theoretical investigations of periodic operation, up to now little attention has been paid on the effect of this novel operation mode on the selectivities of consecutive or parallel reactions. It is still necessary to further develop a novel dynamic mathematic model that considers the feed/drainage behavior and to simulate the effect of the periodic operation on the selectivities of consecutive or parallel reactions.

The objective of this research is to investigate the effect of periodic operation of TBR on the conversion and the selectivity of the consecutive reaction by using the hydrogenation of 2-ethylanthraquinone (EAQs) over Pd/Al_2O_3 as a testing reaction, which differs from the reactions reported in the literatures. In addition, attempts are also made to simulate the performance of periodically operated TBR with a dynamic model and thus to provide an effective tool for the further understanding of this operating mode.

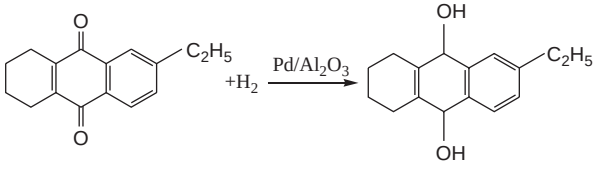
2. Model development

2.1. Testing reaction

Hydrogenation of 2-ethylanthraquinones (EAQs) to 2-ethylanthrahydroquinones (EAHQs) over Pd/Al_2O_3 is one of most important steps in the industrial manufacture of hydrogen peroxide via anthraquinone process, in which 2-ethyl-9,10-anthraquinone (EAQ) and its hydrogenated derivative 5,6,7,8-tetrahydro-2-ethyl-9,10-anthraquinone (THEAQ) dissolved in organic solvents are hydrogenated to the corresponding anthrahydroquinones, i.e., 2-ethylanthrahydroquinone (EAHQ) and 5,6,7,8-tetrahydro-2-ethylanthrahydroquinone (THEAHQ) (Goor and Kunhel, 1989), as follows:



(EAQ) (EAHQ) (1)



(THEAQ) (THEAHQ) (2)

In fact, besides the desired and fast reactions, some secondary reactions (generally deep hydrogenation reactions of anthrahydroquinone, such as hydrogenation of anthraquinone aromatic rings as well as hydrogenlytic reactions) also occur, which lead to the loss of active anthraquinones (EAQ and THEAQ). All the by-reactions can be considered as consecutive to the hydrogenation of EAQs (Drelinkiewicz, 1995). Thus the main reactions taking please in the hydrogenation step can be described as follows:

$$\mathrm{EAQs} \xrightarrow[+H_2]{Pd/Al_2O_3} \mathrm{EAHQs} \xrightarrow[+H_2]{Pd/Al_2O_3} \text{undesired products.} \quad (3)$$

2.2. Model equations

In formulating the mathematical model of unsteady-state operation of TBR, the following fundamental assumptions