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Modeling of bubble column slurry reactor for reductive alkylation of *p*-phenylenediamine

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Abstract

A bubble column slurry reactor (BCSR) model has been developed for the reductive alkylation of *p*-phenylenediamine (PPDA) with methyl ethyl ketone (MEK) to *N*, *N*′-di-secondary-alkyl-*p*-phenylenediamine (Di-amine). This particular reaction system is commercially relevant and involves a combination of parallel and consecutive reactions comprising equilibrium non-catalytic (homogeneous) and catalytic (heterogeneous) steps. The proposed model is based on the 'mixing cell approach'. In this work the mixing cell approach has been extended by including a liquid backflow stream from all but the bottommost mixing cell. The model incorporates the contributions of gas–liquid and liquid–solid mass transfer, heat effects, and complex multistep reaction kinetics. CFD model is used to estimate the extent of backflow among mixing cells and its dependence on operating parameters. The effect of gas and liquid velocities, catalyst loading, inlet PPDA concentration, and temperature on the conversion, selectivity, global rate of hydrogenation, and temperature rise is discussed. The comparison of the current approach with the traditional mixing cell model is discussed. The BCSR model presented here will be useful to provide guidelines for designing and improving overall performance of bubble column reactors.

Keywords: Bubble columns; Reductive alkylation; Mathematical modeling; Kinetics; CFD

1. Introduction

Bubble column slurry reactors (BCSRs), which involve contacting of gaseous and liquid reactants in the presence of suspended solid catalyst particles, are extensively used in several industrial chemical and petroleum refining processes due to better heat and mass transfer. Fine catalyst particles can be used in these reactors, which eliminate intraparticle diffusional resistance, leading to more effective use of the catalyst. The design and scale up of these reactors is of considerable interest, since a number of fundamental and practical issues can be defined that introduce uncertainties in the prediction of reactor performance. Important developments on the reaction engineering analysis of BCSRs were reviewed in earlier work by Shah (1979), Ramachandran and Chaudhari (1983), and Deckwer (1992). More recent reviews had been provided by Saxena (1995), Krishna (2000), and in the monograph of Schumpe and Nigam (1996). Some examples of the commercial applications of BCSRs include Fischer–Tropsch synthesis (Bukur, 1983; Mills et al., 1996; Krishna and Maretto, 1998; Krishna et al., 2001), hydrogenation of adiponitrile (Mathieu et al., 1992), hydrogenation of oils (Bern et al., 1975), and several unsaturated compounds.

In the applications just cited, either a semi-batch or continuous mode is utilized, or in some cases, a continuous flow with recycle operation is followed. The overall performance of such reactors depends on the specific reaction kinetics, mass transfer effects, hydrodynamics, solid catalyst distribution and thermal energy management. In addition, the mixing pattern of gas and

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liquid phases is also important in deciding the overall efficiency of such reactors. While the analysis of multiphase catalytic reactors has been well developed from the theoretical perspective for simple reaction schemes, information on the analysis of reactor performance for industrially useful processes in BCSRs is very limited. In previous work on the modeling of BCSRs, detailed consideration has been given to hydrodynamic modeling, particularly CFD modeling (Krishna and Maretto, 1998; Krishna et al., 2001; Rampure et al., 2007), evaluation of mixing (Govindarao and Chidambaram, 1983), and mass transfer parameters (Kawakami et al., 1981; Dassori, 1998). Although reactor performance models have been proposed for several reactions, such as the Fischer–Tropsch synthesis (Mills et al., 1996; Krishna and Maretto, 1998; Krishna et al., 2001), hydrogenation of glucose (Brahme et al., 1984), and the hydrogenation of butynediol (Jaganathan et al., 1987), in most of these cases, only single reactions with simplified kinetics have been considered. Thakar et al. (2003) have modeled the hydrogenation of maleic acid to tetrahydrofuran (THF) in BCSR, taking into account the distribution pattern of the product THF in gas and liquid phases. Industrial BCSRs typically involve complex multistep catalytic reactions with complexities such as non-linear kinetics, catalyst deactivation, exothermic reactions, and non-uniform distribution of catalyst particles. One such application is the reductive alkylation of amine compounds for the manufacture of higher alkylated (secondary and tertiary) amine derivatives, which find applications as intermediates in fine chemicals and speciality products (Lehtonen et al., 1998). The reductive alkylation reaction goes through a condensation reaction between an amine compound or its precursor and a carbonyl compound or alcohol to form an imine—a Shiff Base—(Ege, 1994), which is hydrogenated in the presence of a metallic catalyst to *N*-alkylated products. Reductive alkylation of nitro or amine compounds has been investigated using a wide range of alkylating agents and catalysts (Greenfield, 1994; Patil et al., 2007).

Most of the previous work on reductive alkylation was focused on catalysis aspects with the aim of improving catalytic activity and selectivity of *N*-alkylated compounds. However, the reaction system has not been studied much from reaction engineering viewpoint. Though, there is an obvious advantage in conducting the condensation and hydrogenation reactions in a single step and effectively drive the equilibrium reaction step to complete conversion, understanding of the reaction engineering aspects is of significant importance to optimize the overall rate of reductive alkylation. There are only a few reports in the literature, which deal with combinations of homogeneous–heterogeneous, non-catalytic–catalytic reactions. Lehtonen et al. (1998) followed by Salmi et al. (1999), developed a semi-batch slurry reactor model and loop reactor model for reductive alkylation of aromatic amines with short chain aldehydes (carbon chain length less than 3) using Pt/C catalyst. More detailed kinetic studies were reported from our group for reductive alkylation of aniline with acetone to *N*-isopropylaniline using Pd/Al_2O_3 catalyst (Roy et al., 2005), and the more complex reductive alkylation of *p*-phenylenediamine (PPDA) with methyl ethyl ketone (MEK) to *N*, *N*′-di-sec-alkyl-*p*-phenylenediamine, using Pt/Al_2O_3 catalyst (Patil et al., 2007), wherein two amine functionalities are available for the alkylation reaction. A schematic of the reaction scheme considered in this work is shown in Fig. 1. In this paper, we have reported a detailed analysis of a BCSR for reductive alkylation of PPDA.

The BCSR model was derived using the detailed kinetics reported in our earlier work (Patil et al., 2007) and mixing cell approach. It incorporates the gas–liquid, liquid–solid mass transfer, heat effects, and complex multistep reaction kinetics. The changes in gas and liquid velocities influence hydrodynamics of BCSR and therefore alter degree of back mixing in liquid phase. Influence of operating conditions on hydrodynamics and liquid phase mixing was quantified using a computational fluid dynamics (CFD) model in the literature (Ekambara and Joshi, 2003; Buwa and Ranade, 2003; Rampure et al., 2007). The model of Rampure et al. (2007) was used for this purpose. Liquid phase backmixing was accounted by including a backflow (obtained using CFD) among mixing cells. The effect of gas and liquid velocities, catalyst loading, inlet substrate concentration, and temperature on the conversion, selectivity, and temperature rise is discussed. The model presented here is useful for developing insight into the effects of various operating parameters on the overall reactor performance.

2. Reactor model

A detailed analysis of a BCSR model has been presented using a mixing cell approach. A mixing cell approach proposed earlier by Ramachandran and Smith (1979), Brahme et al. (1984), and Jaganathan et al. (1987) has been extended in this work by including a liquid backflow stream from all but the bottommost mixing cell. This model incorporated the complexities of reaction kinetics coupled with mass transfer and the thermal effects.

2.1. Intrinsic kinetics

The intrinsic kinetics for the hydrogenation of PPDA to *N*, *N*′-di-sec-butyl-*p*-phenylenediamine with 3% Pt/Al_2O_3 catalyst have been recently studied by Patil et al. (2007) using a batch slurry reactor. Based on this work, the reaction network can be described as shown in Fig. 1. The following types of rate equations for non-catalytic (R_1, R_2, and R_4) steps have been found to adequately describe the individual homogeneous reaction steps involved,

$$R_1 = k_{\mathrm{eq}1} B_l - k_{\mathrm{eq}2} D_l C_{\mathrm{H_2O}}, \tag{1}$$

$$R_2 = k_{\mathrm{eq}3} D_l - k_{\mathrm{eq}4} F_l C_{\mathrm{H_2O}}, \tag{2}$$

$$R_4 = k_{\mathrm{eq}6} G_l - k_{\mathrm{eq}7} H_l C_{\mathrm{H_2O}}, \tag{3}$$

where $k_{\mathrm{eq}1} = k_{\mathrm{eq}1m} C_m$, $k_{\mathrm{eq}3} = k_{\mathrm{eq}3m} C_m$, $k_{\mathrm{eq}6} = k_{\mathrm{eq}6m} C_m$ and

$$C_{\mathrm{H_2O}} = (D_l + 2F_l + G_l + 2H_l + 2P_l),$$

where $k_{\mathrm{eq}1}$, $k_{\mathrm{eq}3}$, $k_{\mathrm{eq}6}$ and $k_{\mathrm{eq}2}$, $k_{\mathrm{eq}4}$, $k_{\mathrm{eq}7}$ were the forward and backward equilibrium rate constants, respectively, for the steps