Chemical Engineering Science 66 (2011) 6028–6038

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

CFD modeling of gas flow in porous medium and catalytic coupling reaction from carbon monoxide to diethyl oxalate in fixed-bed reactors

Xi Gao, Ya-Ping Zhu, Zheng-hong Luo*

Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

ARTICLE INFO

Article history:
Received 4 April 2011
Received in revised form
16 July 2011
Accepted 15 August 2011
Available online 22 August 2011

Keywords:
Porous medium
Multiphase reactors
Packed bed
Mathematical modeling
Catalytic coupling reaction from carbon monoxide to diethyl oxalate
CFD

ABSTRACT

A comprehensive two-dimensional heterogeneous reactor model was developed to simulate the flow behavior and catalytic coupling reaction of carbon monoxide (CO)–diethyl oxalate (DEO) in a fixed-bed reactor. The two-temperature porous medium model, which was revised from a one-temperature porous medium model, as well as one equation turbulent model, and exponent-function kinetic model was constructed for the turbulent velocity scale comparing with laminar flow and simulation of the catalytic coupling reaction. The simulation results were in good agreement with the actual data collected from certain pilot-plant fixed bed reactors in China. Based on the validated approach and models, the distributions of reaction parameters such as temperature and component concentrations in the reactor were analyzed. The simulations were then carried out to understand the effects of operating conditions on the reactor performance which showed that the conduction oil temperature in the reactor jacket and the CO concentration are the key impact factors for the reactor performance.

1. Introduction

As one of the most important alcoholic compounds, ethylene glycol (EG) is widely used, particularly in the field of polyester, synthetic fiber and paint industry, etc. (Eugene and Andre, 2001; Shoaeifar et al., 2007). Recently, a green process for the preparation of EG independent of petroleum, as described in Scheme 1, was developed based on coal (Meng, 2003; Li et al., 2005; Xu et al., 2008a, b). It was first industrialized in China in 2009 (Qian, 2009). This green process is one of the promising methods to convert coal to high-value chemicals (UOPLLC, 2002). Its key part is the coupling reaction, which is shown in

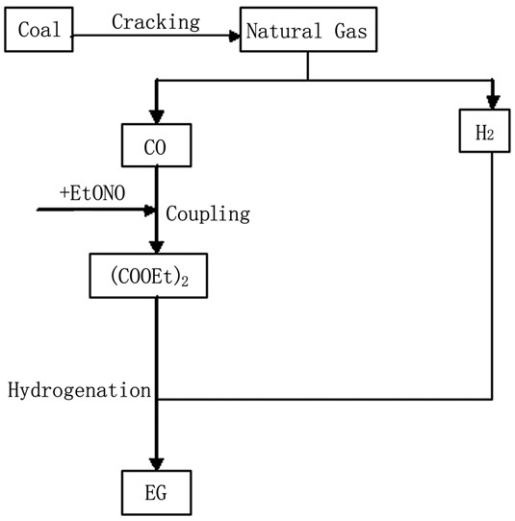
$$2CO+2EtONO \xrightarrow{\text{Coupling reaction}} (COOEt)_2+2NO. \quad (1)$$

Eq. (1) shows that diethyl oxalate ($(COOEt)_2$, DEO) is synthesized through the coupling reaction between carbon monoxide (CO) and ethyl nitrite (EtONO, EN) over supported metal catalyst.

The coupling reaction attracted great interests (Bartley and Charleston, 1987; Chatterjee et al., 2001; Gao et al., 2005; Ji et al., 2009; Le Gall et al., 2001; Shiomi et al., 1989; Wu et al., 2003; Xiao et al., 2000; Xu et al., 1995; Zhang et al., 1995). Most of them focused on the coupling reaction catalyst (Bartley and Charleston, 1987; Shiomi et al., 1989; Wu et al., 2003; Xu et al., 1995; Zhang et al., 1995) and mechanism (Chatterjee et al., 2001; Gao et al., 2005; Ji et al., 2009; Le Gall et al., 2001; Xiao et al., 2000). There are still few studies on the coupling reactors, particularly about the fluid dynamics in these reactors, which can be used to evaluate the reactor performance. Recently, Xu et al. (2008a, b) established a fixed-bed reactor model for the catalytic coupling reaction of CO–DEO. In their study, the gas concentration, temperature and pressure profiles along the axial direction inside the reactor were obtained. However, the usual assumption to model fixed-bed reactors of plug flow was still retained. In addition, Wang et al. (2000) developed a two-dimensional fixed-bed reactor model of coupling reactor of CO–DEO by using advanced software tools, Aspen and Pro-II. However, the special hot spots and their positions cannot be obtained accurately via their reactor models. In addition, the hot spot temperature obtained via the reactor model with ignoring any side reactions cannot reflect the practical situation very well. In practice, the above reactor performance including hot spot information can be predicted via modern computational fluid dynamics (CFD) model. On the other hand, the reactors mentioned above are both fixed-bed reactors, which play a very important part in the chemical industry (Nijemeisland and Dixon, 2004a). Some reactor models were constructed to examine reactor operation parameters. Unfortunately, in present open reports (Bub et al., 1980; Jess et al., 1999), the usual approach to model fixed bed reactors assumes plug flow and effective transport mechanisms. Recent works (Calis et al., 2001; Jiang et al., 2001) suggest that the better predictions of the

* Corresponding author. Tel.: +86 592 2187190; fax: +86 592 2187231.
E-mail address: luozh@xmu.edu.cn (Z.-h. Luo).

0009-2509/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2011.08.031



Scheme 1. A green process for the preparation of EG independent of petroleum.

reactor performance can be obtained for slim tubes if the radial variation of the axial flow component is included. However, effective parameters need to be estimated. The good predictions of the measured reactor performance profiles can only be obtained if an effective viscosity is incorporated.

As described above, the modern CFD model and the exponential growth of computer power are bringing simulations of fixed-bed flow into reality. It is now feasible to obtain detailed flow fields in fixed beds. Furthermore, the CFD is an emerging technique and holds great potential in providing detailed information of the complex fluid dynamics (Ding and Gidspow, 1990; Nijemeisland and Dixon, 2001; Tian et al., 2007a,b). Up to now, considerable attention has been devoted to the application of CFD in fixed-bed reactors (Eu Toit et al., 2006; Guardo et al., 2004; 2005; 2006; Lan et al., 2009; Lopes and Quinta-Ferreira, 2010a, b; Jafari et al., 2008; Jakobsen et al., 2002; Natarajan et al., 2005; Nijemeisland et al., 2004b; Nikačević et al., 2009; Taskin and Dixon, 2008). For instance, Nijemeisland and Dixon (2004a) studied the relationship between the local flow field and the local wall heat flux in a packed bed of spheres. In their work, the CFD was used as a tool to obtain the detailed velocity and temperature fields, when gas flow through a periodic wall segment test cell. Guardo et al. (2005) used the CFD as a simulation tool based on the Eulerian–Eulerian approach to obtain a more detailed view of the fluid flow and heat transfer mechanisms in fixed-bed reactors. This study presented a comparison between the performance in flow and heat transfer estimation of five different RANS turbulence models in a fixed-bed. In practice, most of the early modeling efforts in this field are regarding the fluid flow and heat transfer in gas–solid two-phase fixed-bed reactors. According to the best knowledge of us, so far, there was no open report regarding the application of CFD to the fixed-bed for the catalytic coupling reaction of CO–DEO. On the other hand, generally, due to the complexity of flow shapes in fixed-bed reactors, two CFD methods were applied to simulate the flow in fixed-bed reactors in the past. One handles the fixed-bed reactor as a porous medium or applies the assumption of a quasi-homogeneous reactor model (Jakobsen et al., 2002). Therefore, the reactions occurring in the reactor can be handled as a source item of the continuity equations. Using the method, one cannot obtain the micro-mechanism of liquid flow and transportation. The other solves directly the governing equations of liquid flow and transportation in complex pipelines, which does not simplify the flow shapes and the governing equations. Therefore, by using the direct solution method, a precise and microcosmic fluid flow field in the fixed-bed reactor can be obtained. However, this method needs complex computation meshes and boundary conditions (Calis et al., 2001; Nijemeisland and Dixon, 2004a; Petre et al., 2003).

In this work, based on the first CFD method mentioned above, a comprehensive two-dimensional heterogeneous CFD reactor model incorporating an exponent-function reaction kinetic model is applied to study the flow behavior and catalytic coupling reaction of CO–DEO in a fixed-bed reactor. A one-equation turbulent model suggested by Spalart and Allmaras (1992) is used for the turbulent velocity scale in the fixed-bed reactor. The solid energy equation and heat transfer equation are added into the porous medium model, thus the old one-temperature model is changed into two-temperature model. The CFD model is validated with the actual data collected from certain pilot-plant fixed bed-reactor (Xu et al., 2010) and some reaction parameter distributions in the reactor are also obtained via the above model.

2. Simulation of fixed-bed reactor and coupling reaction

Since Li et al. (2005) and Xu et al. (2010) have experimentally investigated the coupling reaction of CO–DEO in a fixed-bed reactor, the fixed-bed reactor described in their work (Li, et al., 2005; Xu et al., 2010) is selected as the object of our simulation. Referring to reference (Xu et al., 2010), the selected reactor has an inner diameter of 0.027 m and a length of 3 m. The reactor can be divided into three zones. Zone I and Zone III are used for preheating the feed gas and cooling the products, respectively. Zone II is in the middle section of the reactor where reactions occur. More detailed information regarding the fixed-bed reactor configurations is provided in Fig. 2.

On the other hand, as described earlier, the coupling reaction takes place over the supported metal catalyst in a fixed-bed reactor where the spheric catalyst particles of the same size are filled along the axis direction. The gaseous EN and CO are continuously fed into the reactor, and react over the solid catalyst particles to produce gaseous DEO and by-products. Therefore, the reacting system can be considered as a gas–solid two-phase system.

3. CFD model for the fixed-bed reactor

In order to make the simulation meet the demand of engineering, the catalyst particles in the bed are assumed as a continuous porous medium, which in CFD is modeled as a fluid region with extra terms in the momentum balance to allow for additional resistance to flow. However, the default solution of energy equation for the porous medium is based on one-temperature model in FLUENT 6.3.26, giving only an effective thermal conductivity for the porous region. It suggests that the temperature of solid phase equals that of gas phase due to the local thermal equilibrium between the gas–solid two phases. Obviously, it does not accord with the practical reactor. Therefore, the solid energy and heat transfer equations are added into the porous medium model, thus the old one-temperature porous medium model is changed into two-temperature porous medium model.

Moreover, due to the complexity of the fluid flow in porous medium, the turbulent model is thoroughly discussed and simplified in the section. The detailed equations are presented in the following sections.