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Modeling for the catalytic coupling reaction of carbon monoxide to diethyl oxalate in fixed-bed reactors: Reactor model and its applications

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ABSTRACT

A two-dimensional (2D) pseudo-homogeneous reactor model was developed to simulate the performance of fixed-bed reactors for catalytic coupling reaction of carbon monoxide to diethyl oxalate. Reactor modeling was performed using a comprehensive numerical model consisting of two-dimensional coupled material and energy balance equations. A power law kinetic model was applied for simulating the catalytic coupling reaction with considering one main-reaction and two side-reactions. The validity of the reactor model was tested against the measured data from different-scale demonstration processes and satisfactory agreements between the model prediction and measured results were obtained. Furthermore, detailed numerical simulations were performed to investigate the effect of major operation parameters on the reactor behavior of fixed bed for catalytic coupling reaction of carbon monoxide to diethyl oxalate, and the result shows that the coolant temperature is the most sensitive parameter.

Keywords: Multiphase reactors; Mathematical modeling; Kinetics; Fixed-bed reactor; Catalytic coupling reaction

1. Introduction

As one of the most important alcoholic compounds, ethylene glycol (EG) is widely used in organic synthesis, particularly in the polyester, synthetic fibre and paint industry, etc. (Eugene and Andre, 2001; Shoaeifar et al., 2007). Recently, a green process for the preparation of EG independent of petroleum described in Scheme 1 was developed based on coal (Li et al., 2005; Meng, 2003; Xu et al., 2008a) and 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 catalytic coupling reaction, which is shown in Eq. (1):

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

Eq. (1) shows that the coupling reaction is the synthesis of diethyl oxalate ($(COOEt)_2$, DEO, $(COOC_2H_5)_2$) from carbon monoxide (CO) and ethyl nitrite (EtONO, EN, C_2H_5ONO) over supported metal catalyst. On the other hand, catalytic coupling reactions can be accomplished in various types of reactors, such as autoclave, fluidized-bed reactor, or fixed-bed reactor (Cheimarios et al., 2010; Dudukovic, 2010; Hillestad, 2010; Meng et al., 2004). The last one plays a very important part in the chemical industry and is certainly the most important at present (Nijemeisland and Dixon, 2004; Nikačević et al., 2009). In practice, for the catalytic synthesis of DEO and the further synthesis of EG reported in China, the selected reactor is fixed-bed (Qian, 2009; Xu et al., 2010).

On the other hand, it is well known that the economic viability of DEO conversion is determined by capital costs and average product price (Qian, 2009). In this respect, the manufacture of DEO is by far the most capital-intensive of a DEO conversion plant. Therefore, the catalytic coupling reaction of CO to DEO should aim at utilizing reaction materials as efficiently as possible, and selectivity considerations are then extremely important in the design of the catalytic coupling reaction section. To achieve an optimum performance for the complete process, the catalyst and the reactor should be comprehensively optimized (Wang et al., 2003). Obviously, due

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