Kinetic studies in a batch reactor using ion exchange resin catalysts for oxygenates production: Role of mass transfer mechanisms

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Abstract

Oxygenated compounds are usually produced by a reversible liquid phase reaction using ion exchange resins with a bidisperse pore structure as catalyst. Mass transport is mainly controlled by diffusion through the macropores and the mass transfer resistance in the gel microspheres is negligible. Therefore, in this paper a mathematical model of the batch reactor considering diffusion of the species in the external film and then macropore diffusion inside the particle and reaction in the gel microspheres was developed. The numerical solution is implemented through the numerical package PDECOL and detailed explanations of the procedure used are presented. The model was applied to the diethylacetal synthesis using ethanol and acetaldehyde as reactants and Amberlyst 18 as catalyst. The experimental data are fitted with a two-parameter model based on a Langmuir–Hinshelwood rate expression in order to get the true reaction kinetics. The influence of the mass transfer mechanisms is evaluated in terms of the effectiveness factor history during the transient state of the batch reactor. The values of the effectiveness factor calculated at equilibrium with the batch reactor model are compared with those calculated from a steady state infinite bath model.
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1. Introduction

Most industrial chemical processes are catalytic, and therefore the importance and economical significance of catalysis is enormous. More than 80% of the present industrial processes established since 1980 in the fine chemical, petrochemical and biochemical industries use catalysts (Tirronen and Salmi, 2003; Chaudhari and Mills, 2004). The increasing demand for liquid fuels is the driving force for the petroleum industry. However, there is a growing interest in reducing dependence on petroleum and increasing the use of renewable resources for fuel and organic chemicals

production (Embree et al., 2001). To satisfy high performance engines and more and more strict exhaust emission standards, modern gasoline and diesel must meet given specifications which can vary from country to country. The octane and cetane ratings are one of the most known measures of gasoline and diesel quality, respectively. In order to achieve an acceptable octane number, oxygenates like methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE) or tertiary amyl methyl ether (TAME) are added to gasoline to ensure clean combustion. Acetals, and particularly diethylacetal, have been under consideration as oxygenated additives to diesel fuel because they drastically reduce the emission of particles and NO_x while keeping or improving the cetane number and helping in the combustion of the final products, without decreasing the ignition quality (Boennhoff, 1980, 1983; Golubkov and Golubkov, 2002; Laborde, 2003). These oxygenate compounds are commonly produced by a liquid phase reversible

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Table 1
Some experimental investigations of oxygenates production in the literature using acid ion exchange resins

Source	Experimental apparatus	Product	Catalyst
Ali and Bhatia (1990)	Fixed bed catalytic reactor	MTBE	A15
Rehfinger and Hoffmann (1990)	Continuous stirred tank reactor	MTBE	A15
Caetano et al. (1994)	Continuous stirred tank reactor	MTBE	A18
Zhang and Datta (1995)	Upflow integral reactor, continuous	MTBE	A15
Fite et al. (1994)	Differential tube reactor	ETBE	Lewatit K2631
Oost and Hoffmann (1996)	Continuous flow recycle reactor	TAME	Lewatit SPC 118
Fite et al. (1998)	Continuous upflow packed-bed reactor	MTBE	Bayer K2631
Ziyang et al. (2001)	Fixed bed catalytic reactor	MTBE	A15
Pääkkönen and Krause (2003)	Continuous stirred tank reactor	TAME	A16, A35, XE586
Boz et al. (2004)	Fixed bed catalytic reactor	TAEE	A15
Ferreira and Loureiro (2004)	Batch stirred tank reactor	TAME	A15

reaction in acid medium. Because standard ion exchange resins are insoluble acids, they can be used with advantage in many organic reactions where an acidic catalyst is required. Special macroporous sulphonic resins are used for oxygenates production, as shown in Table 1.

Catalysis with acid ion exchange resins has the following advantages over the use of liquid acids:

- a higher local concentration of H$^+$ ions;
- no corrosion;
- possibility of use in continuous processes;
- less secondary reactions;
- easy separation from the reaction medium.

The macroreticular ion exchange resins show bidisperse pore distribution (Quinta-Ferreira and Rodrigues, 1993; Caetano et al., 1994; Ihm et al., 1996). Macroporous resins are characterized by micropores of 0.5–2 nm and macropores of 20–60 nm, depending on the degree of cross-linking (de Dardel and Arden, 2002). The reactant species should first diffuse through the macropores to the external surface of microspheres and then penetrate into the gel phase.

The adsorption and reaction processes over catalysts with bidisperse pore size distribution have been widely studied in the literature. The heterogeneous catalysis processes are regulated by transport phenomena (external and internal diffusion), the adsorption and the reaction at the solid surface. The mass transfer effects in bidisperse catalysts are due to three main mechanisms: mass transfer of species between the bulk fluid phase and the external surface of the stationary phase particles (external mass transfer); diffusive migration through the pores inside the particles (internal pore diffusion); and surface diffusion. The internal pore diffusion may occur by molecular diffusion and Knudsen diffusion (for gas phase), depending on pore size, adsorbate concentrations and other conditions. For resins the microspheres are a gel phase and therefore the mass transfer mechanism that should be considered is the gel diffusion, as shown in Fig. 1.
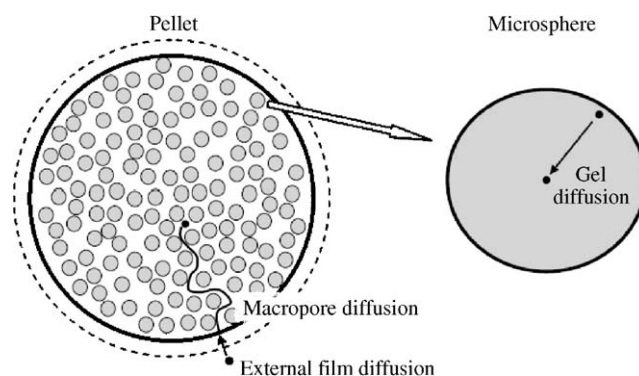

Fig. 1. Schematic representation of the mass transfer mechanisms in a particle of a resin with bidisperse pore structure.

Many authors have developed several models to describe the transport phenomena inside a particle with a bidisperse pore structure. The first and more used model was developed by Ruckenstein et al. (1971), who considers a spherical macroporous pellet to be an assembly of small microspheres. The adsorbate diffuses into macropores, adsorbs on the macropore walls, and also diffuses into the micropores and is adsorbed there. Recently, this model was used to determine the effectiveness of bidisperse catalysts (Leitão et al., 1994), to study adsorption induced convection in the macropores of a bidisperse adsorbent particle (Taqvi et al., 1997). Later, an equivalent model was adopted including gel microspheres diffusion, which considers the microspheres as homogeneous gel particles where the adsorbed phase diffuses (Ruthven and Loughlin, 1972).

Turner (1958) proposed a model structure where the solid network is described by the branched micro–macropore model, including macropores for the transport and micropores to provide capacity of adsorption or reaction, which was also used later by Villermaux et al. (1987). This model was also applied for the analysis of diffusion and reaction in a catalyst with a bidisperse pore structure (Tartarelli et al., 1970). Recently, the Turner structure of a bidisperse model was adopted to study adsorption, because of its simplicity;