Resumo

O efeito da convecção intraparticular em reacções irreversíveis, de 1ª ordem, isotérmicas com variação do número de moles foi analisado em catalisadores de poros-largos com geometria de placa plana. Um modelo, que tem em conta a convecção intraparticular e a variação do número de moles e que é valido em todos os regimes difusivos, foi formulado com base no "dusty gas model". O modelo envolve 4 parâmetros: módulo de Thiele, w ; razão entre a difusividade de Knudsen e a difusividade molecular efectiva, a ; razão entre momento viscoso e difusividade molecular , b ; e queda de pressão externa normalizada, Δf .

Estudou-se o problema de difusão, reacção de 1ª ordem e convecção forçada em catalisadores de poros largos com geometria de cilindro finito. O efeito da convecção no factor de eficiência foi analisado e obtida uma relação para a difusividade efectiva aumentada. Foi ainda obtida uma relação de equivalência entre as dimensões características da placa plana e do cilindro finito.

A difusividade intraparticular foi medida pelo método cromatográfico para catalisadores de poros largos com geometria de cilindro finito, cilindro oco e esfera. Foi obtida uma relação de equivalência entre o cilindro oco e a placa plana.

A cinética de oxidação do etileno a óxido de etileno num catalisador Ag/a -Al_2O_3 foi medida num reactor de Berty e aplicada à simulação dum reactor de leito fixo.

Abstract

The effect of intraparticle forced convection on a heterogeneous reaction within a catalyst pellet was studied. The extended dusty gas model was used to describe mass transport for a first-order, irreversible, isothermal reaction with mole changes within a slab geometry catalyst pellet. Four dimensionless parameters are introduced and studied: the Thiele modulus, f ; the ratio between Knudsen and effective molecular diffusivities, a ; the ratio between viscous momentum and effective molecular diffusivity b ; and the normalised external pressure drop, Δf . A general model which considers both intraparticle convection and mole changes for isothermal first-order reaction in porous catalyst, valid in all diffusion regimes, was derived.

Forced intraparticle convection in a finite cylinder porous catalyst particle was studied. An analytical solution for steady state, simultaneous diffusion, convection and reaction has been obtained and the effect of intraparticle convection on the catalyst performance, i.e., its effectiveness factor, was analysed. The relationship for the augmented intraparticle effective diffusivity and an equivalence ratio between the slab and the finite cylinder characteristic dimensions, valid in the whole range of Thiele modulus, have been obtained.

Mathematical models for solid cylinder and hollow cylinder pellets, where intraparticle convection was considered, have been established and solutions in the Laplace domain have been obtained. Consequently, the equivalence between the hollow cylinder and the slab characteristic dimensions was presented for the first-order-reaction/diffusion/convection problem. A modified chromatographic method has been developed to measure the intraparticle diffusivity in solid cylinder pellets. The axial dispersion of the column packed with the hollow cylinder pellets was determined and a correlation for the Peclet number versus Reynolds number has been obtained. Intraparticle convection was measured with large-pore sphere pellets which present a "foam structure" by using the conventional chromatographic method. Intraparticle Peclet numbers and the permeability of this pellet were determined.

The kinetics of ethylene oxidation over α -alumina supported commercial silver catalysts has been studied with a Berty reactor. Rate equations for the ethylene oxidation for gas mixtures containing excess oxygen was determined. These rate equations can be used under the experimental conditions of this work. The selectivity of the reaction has been studied.

The reaction of ethylene oxidation in a fixed-bed reactor packed with silver catalysts supported in α -alumina was studied experimentally. A mathematical model in which intraparticle diffusion is considered was proposed. The performance of the reactor was simulated. The effects of intraparticle convection on the results of the reaction were discussed.