

Multi-component mass transfer in a single particle during gaseous propylene polymerization

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Received 08 February 2006; accepted 30 October 2006

Mass transfer in the growing catalyst/polymer particle is modeled with dusty gas model (DGM), while the particle growth is described with Polymeric Flow. A Thiele modulus defined in terms of diffusion combined with viscous flow, is called viscous modulus, and used to analyze the dominating mechanism for mass transfer when there is an additional transport of reactant (convection) along with diffusion in a single reacting particle. Addition of high or low molecular weight inert/diluent gas affects mixture diffusivity and thus decreases or increases reaction rate respectively. Both propylene-N₂ and propylene-C₃H₈ systems, which are commonly employed in industry, are studied. Effect of low molecular weight inert is studied with propylene-He system. Porosity and pore size effect on reaction rate is also discussed.

Keywords: Mass transfer, Polymeric flow dusty gas model (PF_DGM), Reaction rate, Viscous modulus

IPC Code: C08F2/34

Introduction

For the porous catalyst particles, in which mean free path of molecule is of the order of pore size, mass transfer can be conveniently described by the dusty gas model (DGM)^{1,2}, which is of considerable interest in a variety of fields of engineering such as catalysis, membrane technology, earth sciences etc. Macroporous materials are often used in membrane technology, and mass transfer limitations become important and influence overall permselectivity³. In multicomponent system, interaction between different species and pressure gradients during reaction exists. Mathematical description of combined effects of multicomponent mass transfer in macro and mesoporous media can be complex. A mixed mode of transport leads to higher predicted mass fluxes than the diffusion alone⁴. Do & Do⁵ observed that viscous flow can enhance the adsorption process due to dragging effect of species into pores of activated carbon. A significant influence of the choice of inert/diluent (helium-ethane and N₂-ethane) was

shown on uptake fraction of ethane. Bulk diffusion of helium-ethane is 4 times higher than in nitrogen-ethane, leading to higher uptakes when helium is used as inert gas. A similar concept is applied to catalytic olefin polymerization to study the influence of inert/diluent on the reaction rate. In gas phase polymerization of propylene, porous catalyst is fed into the fluidized bed reactor, on which polymerization takes place and solid polymer is formed.

This paper presents transport of the gaseous monomer with modified Thiele modulus called viscous modulus in a single polymerizing particle. The growth of polymer particle is modeled in the gas phase using polymeric flow⁶ and the multi component mass transfer in that growing particle (monomer along with inert diluents) is modeled using Maxwell-Stefan approach (in the original polymeric flow model, mass transfer is modeled with Fick's diffusion), which is described as polymeric flow dusty gas model (PF_DGM)⁷.

Proposed Model

Mass balance for a component i , in spherical coordinates and assuming spherical symmetry, is given by

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$$\frac{\varepsilon}{R_g T} \frac{\partial(x_i P)}{\partial t} + \frac{1}{r^2} \frac{\partial(r^2 N_i)}{\partial r} = -(1-\varepsilon) R_{pi} \quad x_i=1,2 \quad \dots (1)$$

where $R_p = k_{pi} A M_i$

Flux term for multi-components in DGM is expressed as

$$\begin{aligned} & \frac{P}{R_g T} \frac{\partial x_i}{\partial r} + \frac{x_i}{R_g T} \left(1 + \frac{B_0 P}{\mu_{geff} D_{i,Kn}^e} \right) \frac{\partial P}{\partial r} \\ & = -\frac{N_i}{D_{i,Kn}^e} + \sum_{\lambda \neq i} \frac{x_i N_\lambda - x_\lambda N_i}{D_{ij}^e} \quad \dots (2) \end{aligned}$$

Flux term for the single component in DGM can be written as

$$N = -\left(D^e + \frac{B_0 P}{\mu_g} \right) \frac{1}{R_g T} \frac{\partial P}{\partial r} \quad \dots (3)$$

Structural or viscous flow parameter is given by

$$B_0 = \frac{\varepsilon d^2}{\tau' 32} \quad \dots (4)$$

where, ε being porosity, τ' is tortuosity and d is the pore diameter.

Substituting flux term of single component in mass balance for steady state gives

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(\left(D^e + \frac{B_0 P}{\mu_g} \right) r^2 \frac{1}{R_g T} \frac{\partial P}{\partial r} \right) - (k_p A) \frac{P}{R_g T} = 0 \quad \dots (5)$$

Eq. (5) is valid for intermediate regime, where diffusion and convection are important. If diffusion is only mechanism, then Thiele modulus for a spherical particle based on first order reaction rate is given by

$$\phi_T = \frac{R_o}{3} \sqrt{\frac{k_p A_o}{D^e}} \quad \dots (6)$$

For intermediate regimes, modulus can be described as

$$\phi_v = \frac{R_o}{3} \sqrt{\frac{k_p A_o}{(D_i^e + B_0 P / \mu_g)}} \quad \dots (7)$$

In multicomponent mass transfer for two-component system, flux term can be written explicitly from Eq. (2), as follows⁴:

$$\begin{aligned} N_1 = & -\frac{P}{R_g T} \frac{D_{1,Kn} D_{12}}{(D_{12} + x_1 D_{2,Kn} + x_2 D_{1,Kn})} \nabla x_1 \\ & - \frac{x_1}{R_g T} \left[\frac{D_{1,Kn} (D_{12} + D_{2,Kn})}{(D_{12} + x_1 D_{2,Kn} + x_2 D_{1,Kn})} + \frac{B_0 P}{\mu_{geff}} \right] \nabla P \quad \dots (8) \end{aligned}$$

Flux for the second component can be simply obtained by interchanging 1 and 2 in Eq. (8). For two component mixture, $D_{12}=D_{21}$. In the case of multi-component system, diffusion contribution comes from the effective diffusivity of gas mixture, and Knudsen diffusivities of the pure components. This is very interesting situation in the case of multicomponent mixture, composed of at least one reactant and one inert or less reactive component. The inert or less reactive accumulates in the particle (enrichment effect) due to consumption of the more reactive reactant further affecting the reaction rates. In case of two component mixture, bulk diffusion of gas mixture depends on molecular weights of individual gases and also on atomic diffusion volumes of gases as given by the Fuller method, as⁸

$$D_{i,j}^0 = 0.00101 \frac{T^{1.75}}{P^1 (V_i^{1/3} + V_j^{1/3})^2} \sqrt{\frac{M_{iw} + M_{jw}}{M_{iw} M_{jw}}} \quad \dots (9)$$

Eq. (9) shows that a heavier hydrocarbon like propane will diffuse slowly compared to an inert gas like helium or nitrogen, but dependence is not linear in terms of molar mass or volume. Diffusivity (D^0) of the two gas mixtures (70% propylene, 30% diluent) at atmospheric pressure and 343 K is as follows: Propylene-He, 0.5089; Propylene-N₂, 0.1554; and Propylene-C₃H₈, 0.0935 cm²/sec. At higher pressures, bulk diffusivities decreases even further. The extent of the measure of reaction rate can be described by a modulus Eq. (10), viscous modulus, which is similar to the Thiele modulus, but accounts for viscous flow of two components in a particle as

$$\phi_v = \frac{R_o}{3} \sqrt{\frac{k_p A_o}{D^{e*}}} \quad \dots (10)$$

Contribution for D^{e*} in one reactant and one inert system is only due to reactant and given by:

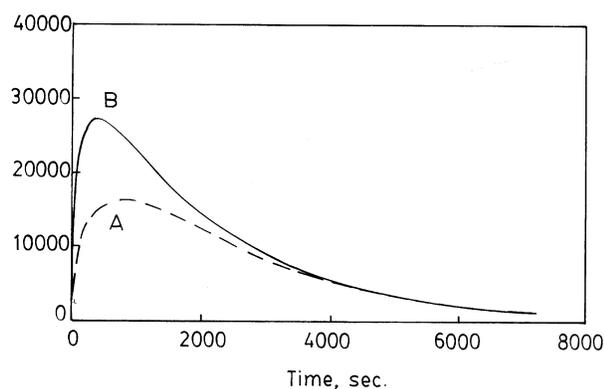


Fig. 1—Predicted reaction rate profiles of propylene polymerization for the intrinsic reaction rate of 40 kg/gcat-h: A) Only with diffusion; B) Diffusion and convection

$$\frac{1}{D_1^{e*}} = \frac{1}{D_{1,Kn}^e} + \frac{x_2}{D_{12}^e} - \frac{x_1 B_o P}{D_{1,Kn}^e \mu_{geff}} \left(\frac{1}{D_{1,Kn}^e + \frac{B_o x_1 P}{\mu_{geff}}} \right) \quad \dots (11)$$

Eq. (11) is derived from Maxwell-Stefan approach⁹. Equations describing particle growth, reaction rate and catalyst's intrinsic reactivity can be found elsewhere¹⁰.

Results and Discussion

Base case simulations are carried out for gas phase polymerization of propylene using following parameters: $k_p A_o$, 763.37 s⁻¹ (pure propylene), 1090 s⁻¹ (70% propylene); P , 28 bars; x_1 (C₃H₆), 0.7; x_2 (N₂, C₃H₈), 0.3; k_d , 0.0005 s⁻¹; ρ , 0.0238 mol/cc; ρ_{cat} , 2.84 g/cc; D^e (pure propylene), 0.0001 cm²/sec; ε , 0.15; τ , 6; R_o , 50 μ m; d , 0.01 μ m; A_o , 10⁻⁵ (for intrinsic reaction rate of 40 kg/g-h) and T , 342 K. Initially, simulations are carried out for a single component (100% propylene) with diffusion alone, and with diffusion and convection in a growing polymer particle. The reaction rates (Fig. 1) for a first order deactivating catalyst with a maximum or intrinsic reaction rate (40 kg/gcat-h) is considerably lower when diffusion is the only transport mechanism. The effectiveness factor (predicted reaction rate/intrinsic reaction rate) increases when both the diffusion and convection are transport mechanisms, and influence of pressure drop on the effectiveness factor cannot be neglected⁴. Catalyst deactivation also shifts the modulus into the non-diffusion limited regime.

In the case of multi-component mass transfer, particularly when the reactant is mixed with an inert, reaction rate is lowered as a function of the amount of inert component present. Reduction in reaction rate is caused by reduction in concentration of the reactant, and also by convective effects. The effect of concentration is excluded in present simulations by estimating the intrinsic reaction rate in terms of the partial pressure of monomer. This study considers reaction rates of 5, 10, 25 and 40 kg/gcat-h with propylene (70%) and diluent (30%: N₂, C₃H₈ or He) under no mass transfer limitations (intrinsic reaction rate). Due to convective flow of gas mixture in pores of particle and accumulation of diluent, gas composition is changing with time in pores affecting the mass transfer.

The effect of convection for homo-polymerization of propylene has been analyzed based on the viscous modulus ϕ_v , for different reaction rates for both propylene-nitrogen and propylene-propane mixtures. For the gas composition (70% propylene, 30% diluent), normalized concentration of both propylene and inert at the center of particle (C_{centre}/C_{bulk}) for different reaction rates are predicted (Fig. 2). Mass transfer limitations could exist at least for first few minutes for this composition at higher reaction rates, whereas the value of x_1 approaches zero at the center of particle and x_2 value to one in Eq. (11); $1/D_i^{e*}$ decreases increasing ϕ_v . At reaction rates of up to 10 kg/gcat-h, diffusion is the dominant mass transfer mechanism, and beyond that convection seems to play an important role in mass transfer for the conditions studied (Fig. 3). In propylene-propane mixture, ϕ_v is higher at 600 seconds compared to 50 seconds indicating that this mixture diffuses slowly leaving the dragged propane due to pressure drop for longer times in the particle.

In some processes, propane is also preferably used as an inert/diluent mixture for two main reasons: (1) Due to presence of propane already in the propylene feed stock from the cracker; and (2) High specific heat capacity of propane. In the reaction rate profiles (Fig. 4) for propylene-He, propylene-N₂ and propylene-C₃H₈ mixtures for the intrinsic reaction rate of 40 kg/gcat-h, flux of propylene is lower in propylene-C₃H₈ mixture. Effect of gas composition on mass transfer (D_i^{e*}) for all the gas mixtures at different times (Fig. 5) indicates that propane

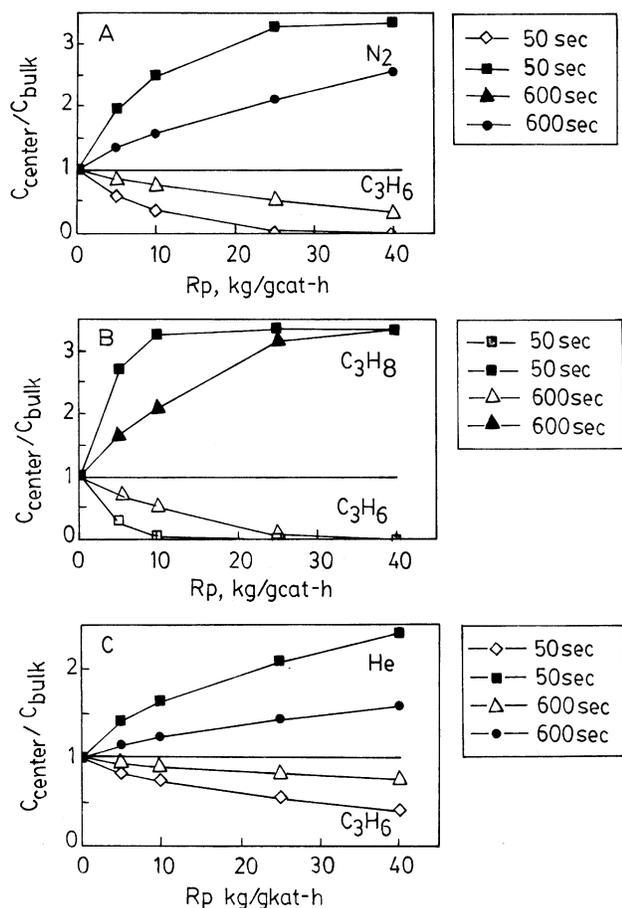


Fig. 2—Model predictions of normalized concentration of propylene and inert at the center of particle with reaction rate at different times for: A) $C_3H_6-N_2$; B) $C_3H_6-C_3H_8$; C) C_3H_6-He

enrichment is more pronounced compared to other inerts. Addition of low molecular weight gas (H_2), which is used as chain transfer agent, also predicts higher reaction rates¹¹. Such a low or high molecular weight gases/inerts can be a choice of diluents in catalytic olefin polymerization depending on the interest.

For mass transport in porous medium, various mechanisms are possible (Fig. 6)¹². For the lowest pore size ($0.01 \mu m$) and for the conditions considered in the present work studied, the Knudsen number (mean free path of the molecule divided by the pore dia) is <1 indicating the viscous flow is important. Nevertheless, this criterion is believed to be very empirical and also no such criterion is reported for multi-component gas mixtures. Krishna & Wessling⁹ suggested viscous selectivity factor, stating relatively large molecules in narrow pores would tend to congregate at the center of the pore exceeding

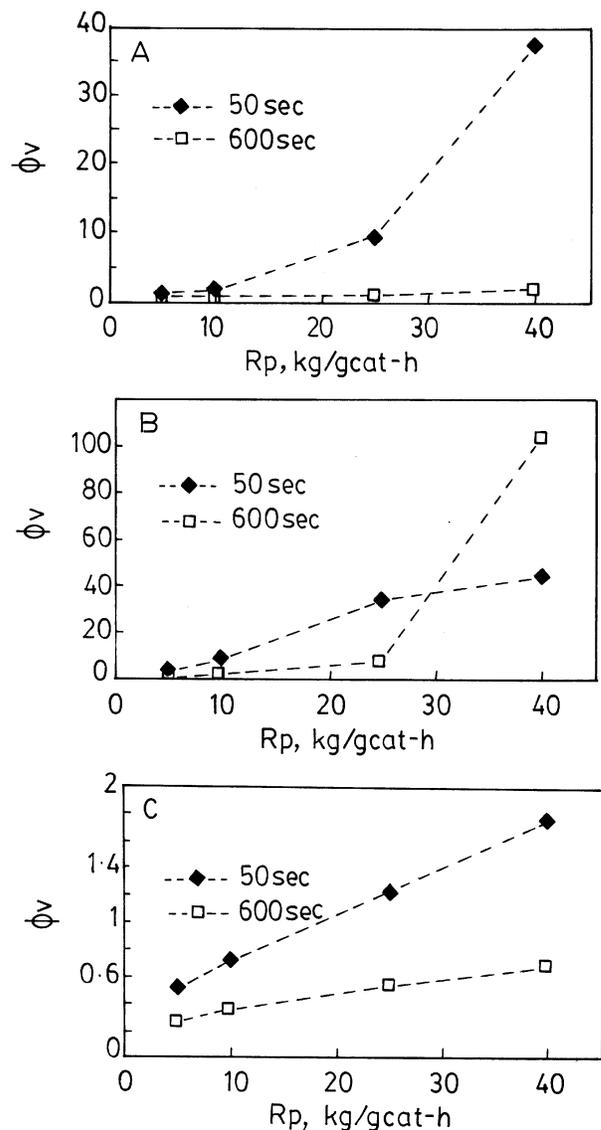


Fig. 3—Viscous modulus (ϕ_v) vs reaction rate for a porous particle at different times for: A) 70% C_3H_6 and 30% N_2 ; B) 70% C_3H_6 and 30% C_3H_8 ; C) 70% C_3H_6 and 30% He

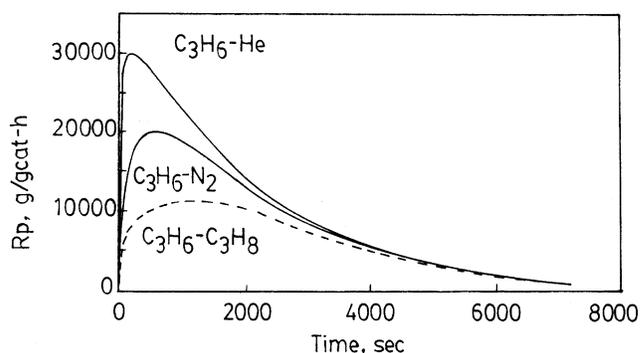


Fig. 4—Reaction rate profiles for the different gas mixtures with fixed composition 70%-30% (for $R_{intrinsic} = 40$ kg/gcat-h)

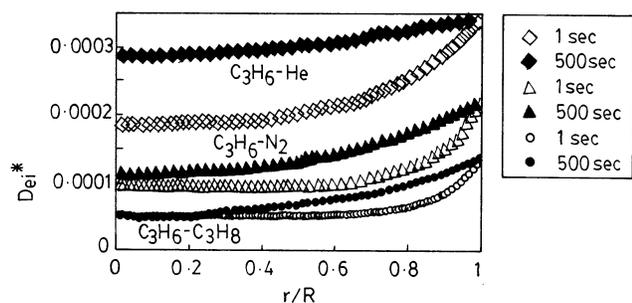


Fig. 5—Effect of gas composition on the monomer mass transfer ($D_{i,r}^*$) in the particle

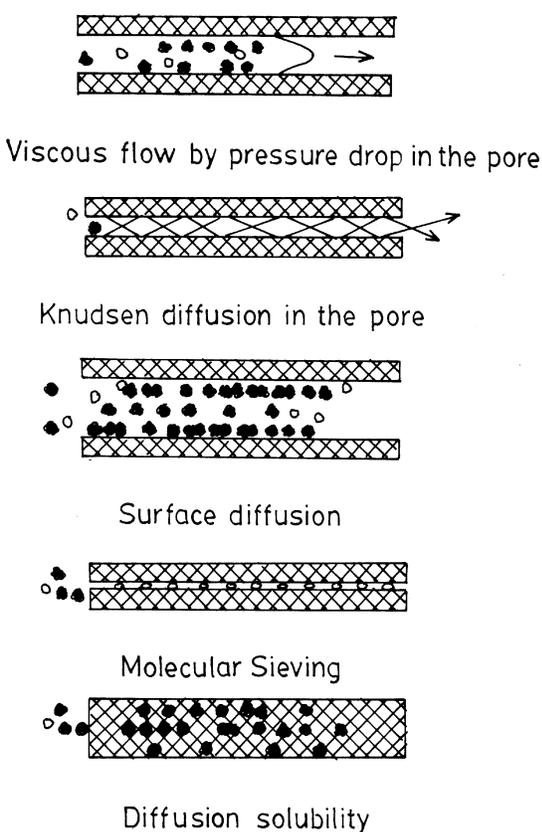


Fig. 6—Schematic of various mass transfer mechanisms¹²

selectivity factor one and other molecules, which stick and slip at the pore walls, have selectivity factor less than one. Considering a pore size of $0.01 \mu\text{m}$ (100 \AA) and propylene, propane, nitrogen and helium molecule sizes (average molecular diameters of 5 \AA , 4.9 \AA , 3 \AA and 2 \AA respectively), viscous flow could be well possible at higher pressures. Due to the lack of availability of viscous selectivity factors and their dependency on the complexity of structure of the matrix, this study did not consider them in present simulations. Also, it is stated that viscous selectivity

effects are important for transport of large molecules such as proteins. As far as the molecules of any gas can be accommodated in the pores, flow of gas can be possible due to pressure drop created by the reaction in porous catalyst particle. Simultaneously, other mode of mass transport occurs as the porous structure is very complicated and one may have continuous pores, dead end and isolated pores. Micropores ($<100 \text{ \AA}$) can exist near the active sites covered by freshly produced polymer. For condensing gases like propylene, surface and solubility diffusion is very important, which may influence the viscous selectivity but depends on the crystallinity and crystal size distribution in the growing polymer particle around the active site. Also, as highly absorbing and reactive gases like propylene are consumed by reaction, concentration of non-absorbing gases like nitrogen increases on the surface forming a blanket, which may increase mass transfer resistance further into the polymer phase. Finally, near the dew point, capillary condensation can reduce mass transfer rate dramatically.

Systematic variation of pore size in the model indicates that pore size distribution doesn't contribute to the mass transfer resistance (Fig. 7A) for a given particle porosity and the conditions studied ($R_{intrinsic} = 40 \text{ kg/gcat-h}$). Similar results are predicted (Fig. 7B) for larger particle size ($R_o = 75 \mu\text{m}$) but the effect of pore size may become significant for even larger particle sizes. In large pores, bulk diffusion is the controlling regime, and whereas in small pores, Knudsen diffusion is the controlling regime. Bulk diffusivities D_{ij}^e are inversely proportional to the system pressure and independent of pore size and so in the bulk diffusion controlled regime the fluxes are independent of system pressure and pore size. On the other hand, Knudsen diffusivities $D_{i,Kn}^e$ are independent of the pressure and directly proportional to the pore size and so the fluxes are directly proportional to the system pressure and pore size. This explains the slightly low reaction rate for the smallest pore size compared to the large pore size studied in the present work, and the effect could be very significant if pore size decreases with increasing particle size. Experimental verification of this phenomenon is reported⁹ for the data of diffusion of helium-neon-argon through a bundle of capillary¹³ using DGM. But the effect of particle porosity has influence on the reaction rate and is also dependent on particle size

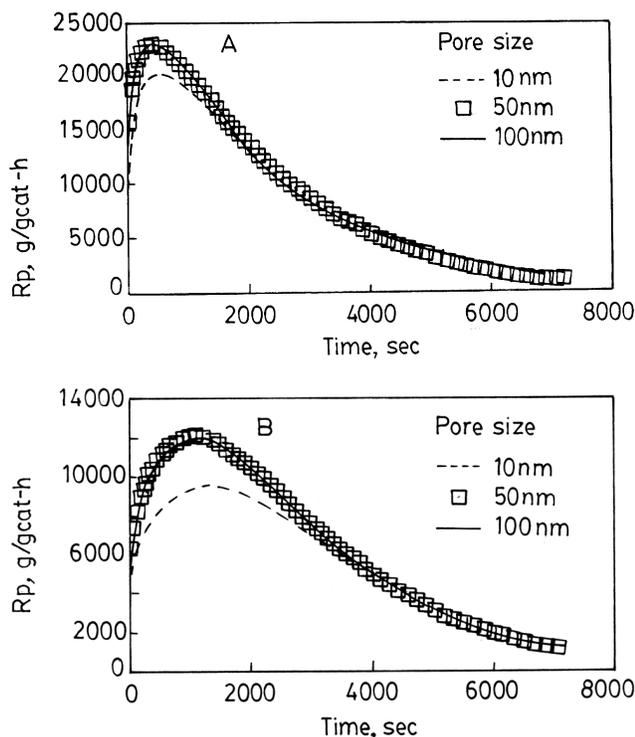


Fig. 7—Effect of pore diameter for a given particle porosity for propylene-nitrogen (70%-30%) gas mixture ($R_{intrinsic} = 40 \text{ kg/gcat-h}$; $\varepsilon = 0.15$) at: A) $R_o = 50 \mu\text{m}$; and B) $R_o = 75 \mu\text{m}$

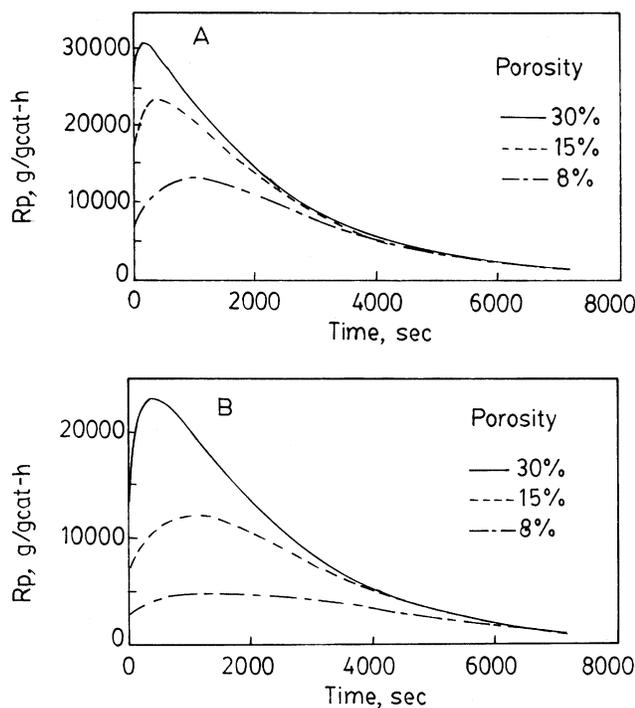


Fig. 8—Effect of particle porosity on reaction rates for a given pore diameter for propylene-nitrogen (70%-30%) gas mixture ($R_{intrinsic} = 40 \text{ kg/gcat-h}$; $d_p = 0.05 \mu\text{m}$) at: A) $R_o = 50 \mu\text{m}$; and B) $R_o = 75 \mu\text{m}$

(Fig. 8). For 50- μm radius particle, reaction rate is influenced to lesser extent by doubling particle porosity, whereas for higher particle size (75 μm), particle porosity plays an important role. Evolution of morphology would be different for different catalysts and depends on pre-polymerization reactor conditions or initial reaction rate¹⁴. So the evolution of particle morphology at the early stages of the reaction either with or without pre-polymerization step will have large influence on the heat and mass transfer phenomena in a growing polymer particle in a fluidized bed reactor.

Conclusions

The proposed mathematical model based on Maxwell-Stefan approach for description of mass transfer helps to understand effect of species interaction on diffusion. A modulus defined with convection and diffusion for a single or two component mixtures is called viscous modulus and used to analyzing the convective effects on reaction rate. Model predicts that pore size distribution has little effect on the reaction rate for the conditions studied, but particle porosity will influence the reaction rate. As the particle size increases further, the effect of pore size and porosity will be higher. The predicted effects should be verified experimentally both quantitatively and qualitatively.

Acknowledgement

One of the authors (UPV) acknowledges Dr U S Agarwal for his intellectual inputs.

Nomenclature

A	Catalyst concentration (based on volume of polymer particle), kgmol m^{-3}
A_0	Initial catalyst concentration, kgmol m^{-3}
B_0	Viscous flow parameter, cm^2
C_{bulk}	Bulk monomer concentration, kgmol m^{-3}
C_{centre}	Monomer concentration at the centre of particle, kgmol m^{-3}
d	Catalyst or polymer particle pore diameter, cm
D_{12}^e	Effective bulk coefficient at the particle level, $\text{cm}^2 \text{s}^{-1}$
$D_{i,Kn}^e$	Effective Knudsen diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$
k_p	Propagation rate constant, $\text{m}^3 \text{kgmol}^{-1} \text{s}^{-1}$
k_d	Deactivation rate constant, s^{-1}
M_i	Monomer concentration ($P/R_g T$), kgmol m^{-3}
M_w	Molecular weight of the monomer, kg kgmol^{-1}
N_i	Monomer Flux, $\text{mol m}^{-2} \text{s}^{-1}$

P	Monomer pressure, Pa
r	Radial location in the growing particle
R_g	Universal gas constant, N m kgmol ⁻¹ K ⁻¹
R_p	Rate of reaction, based on polymer volume, kgmol m ⁻³ s ⁻¹
R_o	Initial radius of the particle, m
t	Time, sec
T	Temperature, K
V	Atomic diffusion volumes
x_i	Mole fraction of gaseous component
ε	Porosity
ϕ_T	Thiele Modulus
ϕ_v	Viscous Modulus
τ'	Tortuosity
μ_g	Monomer viscosity, Pas
$\mu_{g^{eff}}$	Effective viscosity of the gas mixture, Pas

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