Modified mathematical model for gas phase olefin polymerization in fluidized-bed catalytic reactor

Ahmmed S. Ibrehem[a], Mohamed A. Hussain[a,*], Nayef M. Ghasem[b]

[a] Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Chemical & Petroleum Engineering, UAE University, Al-Ain, P.O. Box 17555, UAE

ABSTRACT

A modified model for the gas phase catalyzed olefin polymerization fluidized-bed reactors (FBR) using Ziegler–Natta catalyst is presented in this study. This mathematical model accounts for mass and heat transfer between the bubbles and the clouds without chemical reaction, between the clouds and the emulsion without chemical reaction, and between emulsion and solid with chemical reaction that occurs at the surface of the catalyst particles. The model accounts for the effect of catalyst particles type and porosity on the rate of reaction. In this work, the concentration and temperature profiles in the bubble, and emulsion phases are calculated and the effect of catalyst solid phase on the system is estimated. The effect of important reactor parameters such as superficial gas velocity, catalyst injection rate, and catalyst particle growth on the dynamic behavior of the FBR is investigated and the behavior of mathematical model is compared with the reported models for the *constant bubble size model*, *well-mixed model and bubble growth model*. Moreover, the results of the model are compared with the experimental data in terms of molecular weight distribution and polydispersity of the produced polymer at steady state. A good agreement is observed between our model prediction and the actual plant data.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The general classification of polyethylene semi-batch reactor models has been considered by many previous studies. Generally, three main models exist namely; *constant bubble size model* [1], *well-mixed model* [2] *and bubble growth model* [3].

These reactor models can be divided into homogeneous and heterogeneous categories. The *pseudo-homogeneous polyethylene* models are the simplest to use in catalyst bed batch reactor modeling. The basic assumption made is that the reactor can be described as an entity consisting only of a single (liquid or gas) phase. *On the other hand*, heterogeneous models are used mainly for the case of gas phase polyethylene semi-batch reactors. These use heterogeneous catalysis because of the multi-phase nature of the process (liquid–solid phase or gas–solid phase) and also involve inter-phase mass transfer, heat transfer and chemical reaction [4,5].

Heterogeneous models are used widely especially in polymerization system [5,6]. Current research in this important area can be divided into two parts namely; mathematical models for fixed bed catalyst reactor systems and mathematical models for fluidize bed catalytic reaction for production of polyethylene. Chatzidoukas et al. [4] where the improved heterogeneous model considers the distinction between the gas phase and solid phase. Varma (1981) included mixing in the axial direction. Sala et al. [5] developed a two dimensional mathematical model where concentration and temperature patterns in the reactor can be predicted. Zeman and Amundson [6], Zheng et al. [7], Zavala et al. [8] improved the dynamic optimization of a semi-batch reactor for polyurethane production, Hatzantonis et al. [3] further improved the two-phase model of the polymerization system. In previous works, mass transfer with chemical reaction in fluidized-bed systems either consider all phases (Kunii and Levenspiel, 1969) or the emulsion phase alone (Choi and Ray, 1985; McAuley et al., 1994) [3,7–9].

In this study the contribution in the modified modeling is by including the catalyst phase and considering all three phases as compared to the other models i.e., constant bubble size model, well-mixed model and the bubble growth model. Simulations were also performed to study the effect of superficial velocity and catalyst flow rate in the bubble and emulsion phases. Comparisons with actual plant data at steady state were also performed.

* Corresponding author. Fax: +603 79675319.
E-mail address: mohd_azlan@um.edu.my (M.A. Hussain).

Nomenclature

Ar	Archimedes number [$= d_p^3 \rho_g (\rho_s - \rho_g) g / \mu^2$]
A_{sf}^k	fraction of metal that can form "k" catalyst active
A_B	cross sectional area of bubble phase (m^2)
A_1	cross-sectional area of the bed (cm^2)
C_d^k	concentration of deactivated catalyst active sites (mol/cm^3)
C_{pg}	specific heat capacity of gaseous stream (cal/g/K)
C_{PMi}	specific heat of "I" monomer (cal/mol/K)
$C_{p,pol}$	specific heat capacity of polymer product (cal/g/K)
$C_{A.S}$	adsorbed surface concentration of A in kmol/kg catalyst
$C_{B.S}$	product desorption of B in kmol/kg catalyst
C_B	product concentration (kmol/kg catalyst)
C_V	vacant molar concentration sites (kmol/kg catalyst)
C_{cat}	mass fraction of catalyst in the solid phase
C_{AB}	concentration of monomer gas in bubble phase (kg/m^3)
C_{Ac}	concentration of monomer gas in cloud phase (kg/m^3)
C_{Ae}	concentration of emulsion phase (kg/m^3)
d_{bm}	maximum stable bubble size (cm)
d_p	particle diameter (cm)
d_b	bubble diameter (cm)
D_g	gas self-diffusion coefficient (cm^2/s)
D_n^k	concentration of "dead" copolymer chains (mol/cm^3)
D_{bed}	bed diameter (m)
h	random bed height (m)
H	total bed height (cm)
H_{mf}	bed height at minimum fluidization conditions (m)
H_{bc}	bubble to cloud heat transfer coefficient (cal/m^3/s/K)
H_{ce}	cloud to emulsion heat transfer coefficient (cal/m^3/s/K)
H_{be}	bubble to emulsion heat transfer coefficient (cal/m^3/s/K)
$[H_2]$	hydrogen concentration (mol/m^3)
k_g	gas thermal conductivity (J/m/s/K)
k_i	rate constant of reaction (l/s)
k_A	thermal conductivity between layers of catalyst particles (J/m^2/s/K)
k^n	rate constant of spontaneous reaction (l/s)
k^f	rate constant of chain transfer (l/s)
K_{bc}	bubble to cloud mass transfer coefficient (l/s)
K_{ce}	cloud to emulsion mass transfer coefficient (l/s)
K_{be}	bubble to emulsion mass transfer coefficient (l/s)
K^h	rate constant of chain transfer to hydrogen (l/s)
MFI	melt flow index of polymer (g/10 min)
$[M_e]$	active metal concentration (mol Me/m^3)
$[M_i]$	"I" monomer concentration (mol Me/m^3)
P_A	partial pressure of A in gas phase
P^0	potential active sites (kmol/m^3)
P_0	active sites concentration (kmol/m^3)
PDI	polydispersity index
Q_0	volumetric product removal rate (m^3/s)
r	radius (m)
r_a	rate expression for the active sites (kmol/kg catalyst)
$R_{\mu n,i}^k$	rate expression for live moments
$R_{vn,i}^k$	rate expression for dead moments
R_X^k	reaction rate of species X at "k" catalyst active sites (mol/m^3/s)

S_P^k	concentration of potential "k" catalyst active sites (mol/m^3)
T	temperature (K)
T_b	temperature in the bubble phase (K)
T_{ref}	reference temperature (K)
T_e	emulsion phase temperature (K)
T_w	wall temperature (K)
T_{fs}	temperature of inlet catalyst (K)
T_f	temperature of the feed gas (K)
u_{mf}	minimum fluidization velocity (m/s)
u_e	emulsion gas velocity (m/s)
V	volume (m^3)
Z	bed height (m)

Greek letters

α	ratio between weak to bubble volume
δ_b	bubble phase volume fraction
δ^*	fraction of fluidized-bed consisting of bubbles
$\Delta H_{r \times n}$	heat of reaction (kJ/kg)
ε	void fraction of the bed at minimum fluidized velocity
μ_g	viscosity of gas (g/cm/s)
μ_0^k	live polymer zero
μ_1^k	live polymer
μ_2^k	live polymer
v_0^k	dead polymer
v_1^k	dead polymer
v_2^k	dead polymer
π	constant ratio
ρ_s	solid density (kg/m^3)

Subscripts/superscripts

B	bubble phase
cat	catalyst property
e	emulsion phase
k	type of catalyst active site
mf	minimum fluidization conditions
n	compartment number
ref	reference value
1	monomer gas ethylene
2	monomer gas butane

2. Description of the improved mathematical model

2.1. Fluidized-bed system

In the fluidized-bed system considered here as seen in Fig. 1, the reactant gas enters the bottom of the bed and flows up the reactor in the form of bubbles. As the bubbles rise, mass transfer of the reactant gases takes place between the bubbles and the clouds and between the clouds and the emulsion without chemical reaction. The mass transfer between emulsion and solid with chemical reaction happens on the surface of the catalyst particles.

The model accounts for the type of catalyst particles and catalyst porosity. This is due to their effects on the rate of reaction as shown in Fig. 1. The product then flows back into the bubble and finally exits when the bubble reaches the top of the bed. The rate at which the reactants and products transfer in and out of the bubble affects the product conversion. Literally hundreds of investigators have contributed to what is now regarded as a fairly practical description of the behavior of a fluidized bed;