Multizone Circulating Reactor Modeling for Gas-Phase Polymerization. I. Reactor Modeling

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ABSTRACT: A new gas-phase technology for polyolefin production is being developed to be commercially available for large-scale production between 2004 and 2005. This new technology uses a multilane circulating reactor, which consists of two interrelated zones where two distinct and different fluodynamic regimes are realized, between which the polymer particles are kept in continuous circulation. This article presents a mathematical model for the multilane circulating reactor presenting the typical behavior of the reactor operation and a parameter sensibility analysis. Simulations were conducted for polyethylene production. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1042–1052, 2004

Key words: multilane circulating reactor; modeling; gas-phase polymerization; polyethylene

INTRODUCTION

Gas-phase technology for polyolefin production has been available since the mid-1950s and is widely used for polyethylene and polypropylene production. Since the early fluidized bed reactors from the 1980s, many other successful technology process configurations have been developed to produce polymers with some special properties or to meet property needs. New technologies have been developed to expand the properties for polyolefin resins, and it has been demonstrated that properties could be expanded by conducting polymerization in two or more polymerization steps, each of them under different operating conditions and producing polymers with different molecular weights and compositions. Examples of such technologies for polyethylene are Borstar (Borealis), CX (Mitsui), Hostalen (Elenac), and Spherilene (Basell).

The problem with these two-step processes is that the polymer has low homogeneity of the two (or more) polymer grades and the final polymer particle has a core-shell-like structure [Fig. 1(a)]. Improved polymer grade homogeneity can be attained if the polymer particle could circulate continuously by the two poly-merization steps. In this case, the final polymer particle will have an onion ring structure [Fig. 1(b)].

The new technology that is currently under development by Basell uses a multilane circulating reactor (MZCR), which is similar to a circulating fluidized bed reactor (CFBR), to produce polymers with an onion ring structure. This article will present a mathematical model for the MZCR and will show the typical behavior of the reactor. A parameter sensibility analysis will also be shown to present how each operating and design parameter can change the reactor behavior and polymer characteristic.

MULTIZONE CIRCULATING REACTOR

The concepts for the MZCR and some partial data were reported by Covezzi and Mei,[1] Govoni et al.,[2] and Govoni and Covezzi.[3] The reactor configuration (Fig. 2) provides polymerization in the gas phase in two polymerization zones made by two cylindrical interconnected vertical legs (riser and downer), in which the polymer is circulating continuously.

In the riser section, the polymer flows upward by means of a gas stream under the conditions of fast fluidization or pneumatic transport.[4,5] The gas is fed in the bottom of the section along with polymer particles coming from the downer section and prepolymer or catalyst (made up of active sites). The polymer particles that leave the riser section are transferred to a cyclone positioned in the top of the downer section. In the cyclone, the polymer is separated from the gas stream and falls to the downer section.
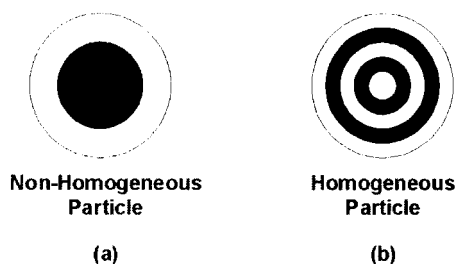
Figure 1 Distribution of the polymer grades within the polymer particle. (a) Particle produced by multiple stage processes. (b) Particle produced by the multilane process.

In the downer section, the polymer flows downward by means of gravity, forming a packed-bed moving downward. The polymer is transferred from the downer to the riser through an L valve (or similar valve) that also is responsible for controlling the solids circulation rate between the sections. The volume of solids in each compartment can be up to 90% in the downer and 40% in the riser. A special characteristic of this reactor is the possibility of operating each section under different operating conditions (pressure, temperature, gas composition), thus producing different polymer grades in each section. This is allowed by introducing a gas feed at the top of the downer section (gas barrier).

The advantage of the MZCR in relation to the multistep processes relies on the improved homogeneity of the two polymer grades in the polymer particles (as said before). This improved homogeneity is welcome in several processes and is critical for materials produced by blow molding or in the production of films where the inhomogeneity of the polymer or impurities can lead to the formation of fish-eyes. Covezzi and Mei[1] and Galli and Vecellio[6] also reported that properties such as impact resistance, mechanical resistance, thermal resistance, impermeability, and others are improved by the use of the MZCR technology. Govoni et al.[2] and Govoni and Covezzi[3] report that the simpler reactor geometry allows broader operating limits being possible to operate at higher pressures than with traditional fluidized-bed reactors (FBR). Therefore, higher concentrations of reagents can be used to enhance productivity. This technology also allows improved conditions for polyethylene copolymers with hexene and octene.

MATHEMATICAL MODELING

The MZCR model that was developed considers two phases in the reactor: gas phase and polymer particles (solids). The model was also divided into two parts: one for the riser and one for the downer section because they operate at different fluodynamics regimes.

The riser model follows the principles of pneumatic transport set by Kunii and Levenspiel.[4] This regime is attained when the gas velocity is higher than the transport velocity of the particles. The regime is established in the riser section by feeding a mixture of gases in the base of the riser. Gas velocity should be set between 5 and 15 m/s. Assuming the conditions for pneumatic transport, the gas can be considered to flow in plug-flow regime throughout the riser and the modeling equations for mass and energy balances for such a condition are given by

$$\frac{dC_i}{dz} = -\frac{Rp_i(1 - \varepsilon^r)}{u_g} = -\frac{Rp_i(1 - \varepsilon^r)}{u_0\varepsilon^r} \tag{1}$$

$$\frac{dT}{dz} = -\frac{\sum_{i=1}^{NC}(-\Delta H)Rp_i(1 - \varepsilon^r)}{[u_sCp^*\rho_p(1 - \varepsilon^r) + u_0\varepsilon^r\sum_i(Cp_iC_i)]} \tag{2}$$

$$Rp_i = \sum_{j=1}^{NC} kp_{ij}C_iY_0\phi_j \tag{3}$$

As with the gas, the polymer particles will also be flowing upward in a plug-flow regime, but at a different velocity because the solid particles will be under the influence of the drag force (promoted by the gas) and the gravity force (due to the particle mass). Thus, the polymer particles will flow at a lower velocity
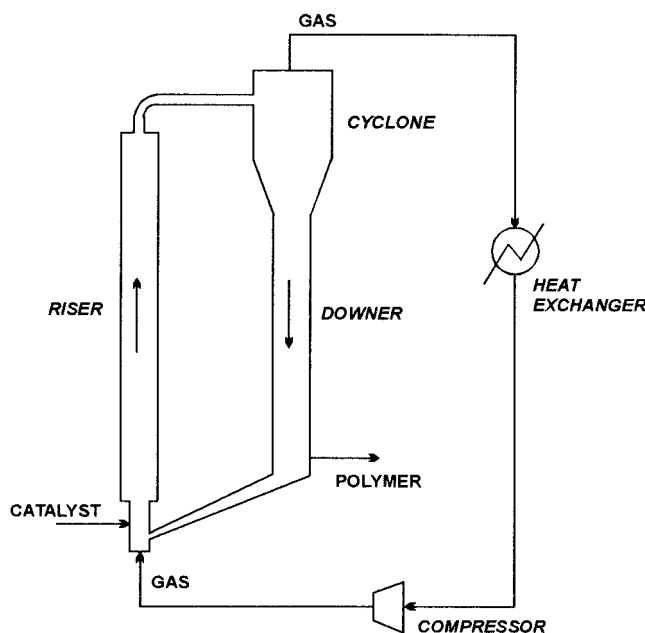
$$U_s = U_g - U_{slip} = U_g - U_t \tag{4}$$

Figure 2 Multizone circulating reactor diagram.

TABLE I
Kinetic Parameters for Ethylene Polymerization (Ziegler–Natta catalyst)
(units in L/mol s)

Formation of active sites (kf)	1.0
Initiation of active sites—Reaction with ethylene (ki_1)	1.0
Initiation of active sites—Reaction with butene (ki_2)	0.14
Propagation—Terminal ethylene with ethylene monomer (kp_{11})	85
Propagation—Terminal ethylene with butene monomer (kp_{12})	2.0
Propagation—Terminal butene with ethylene monomer (kp_{21})	64
Propagation—Terminal butene with butene monomer (kp_{22})	1.5
Chain transfer to ethylene monomer—Terminal ethylene (kfm_{11})	0.0021
Chain transfer to butene monomer—Terminal ethylene (kfm_{12})	0.006
Chain transfer to ethylene monomer—Terminal butene (kfm_{21})	0.0021
Chain transfer to butene monomer—Terminal butene (kfm_{22})	0.006
Chain transfer to hydrogen—Terminal ethylene (kfh_1)	0.088
Chain transfer to hydrogen—Terminal butene (kfh_2)	0.088

The equations for the concentration of active sites in the riser and the moments for the dead and live polymer are given by

$$\frac{dR_0}{dz} = -\frac{kfR_0(1 - \varepsilon^r)}{u_s} \tag{5}$$

$$\frac{dR^*}{dz} = \frac{kfR_0(1 - \varepsilon^r)}{u_s} - \frac{\sum\limits_{i=1}^{NC} ki_i C_i R^*(1 - \varepsilon^r)}{u_s} \tag{6}$$

$$\frac{dY_0}{dz} = \frac{\sum\limits_{i=1}^{NC} ki_i C_i R^*(1 - \varepsilon^r)}{u_s} \tag{7}$$

$$\frac{dY_1}{dz} = [\sum_{i=1}^{NC} ki_i C_i R^* + \sum_{i=1}^{NC}\sum_{j=1}^{NC} kp_{ij} C_i Y_0 \phi_j + \sum_{i=1}^{NC}\sum_{j=1}^{NC} kfm_{ij} C_i (Y_0$$
$$- Y_1)\phi_j + \sum_{j=1}^{NC} kfh_j H_2 (Y_0 - Y_1)\phi_j] \frac{(1 - \varepsilon^r)}{u_s} \tag{8}$$

$$\frac{dY_2}{dz} = [\sum_{i=1}^{NC} ki_i C_i R^* + \sum_{i=1}^{NC}\sum_{j=1}^{NC} kp_{ij} C_i (2Y_1 + Y_0)\phi_j$$
$$+ \sum_{i=1}^{NC}\sum_{j=1}^{NC} kfm_{ij} C_i (Y_0 - Y_2)\phi_j + \sum_{j=1}^{NC} kfh_j H_2 (Y_0$$
$$- Y_2)\phi_j] \frac{(1 - \varepsilon^r)}{u_s} \tag{9}$$

$$\frac{dY_3}{dz} = [\sum_{i=1}^{NC} ki_i C_i R^* + \sum_{i=1}^{NC}\sum_{j=1}^{NC} kp_{ij} C_i (3Y_2 + 3Y_1 + Y_0)\phi_j$$
$$+ \sum_{i=1}^{NC}\sum_{j=1}^{NC} kfm_{ij} C_i (Y_0 - Y_3)\phi_j + \sum_{j=1}^{NC} kfh_j H_2 (Y_0$$
$$- Y_3)\phi_j] \frac{(1 - \varepsilon^r)}{u_s} \tag{10}$$

$$\frac{dQ_k}{dz} = [\sum_{i=1}^{NC}\sum_{j=1}^{NC} kfm_{ij} C_i Y_k \phi_j + \sum_{j=1}^{NC} kfh_j H_2 Y_k \phi_j] \frac{(1 - \varepsilon^r)}{u_s} \tag{11}$$

TABLE II
Operating Conditions Used in the Simulations

|	
Temperature	343 K
Pressure	30 atm
Riser	
Height	5.0 m
Diameter	0.3 m
Gas velocity	5 m/s
Particle velocity	4.2 m/s
Porosity	0.90
Ethylene concentration	0.320 mol/L
1-Butene concentration	0.107 mol/L
Inert concentration (Nitrogen)	0.640 mol/L
Hydrogen concentration (CTA)	0.020 mol/L
Catalyst feed flow rate (make-up of catalyst)	0.20 g/s
Downer	
Height	3.0 m
Diameter	0.3 m
Gas velocity in the downer	0.4 m/s
Porosity	0.15
Gas and polymer physical properties	
Gas density	29.0 g/L
Gas viscosity	0.0109 cP
Gas heat capacity	1.406 J/mol K
Polymer density [density = A − B*(1-butene weight fraction)]	A = 966.0 g/L B = 23.86
Polymer heat capacity	1.839 J/g K
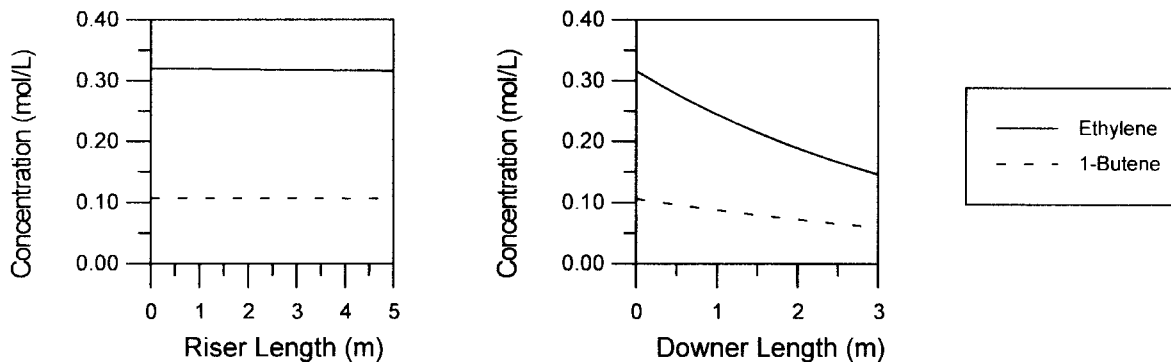
Figure 3 Concentration of monomers throughout the riser and downer sections.

The conditions in the riser depend on a steady flow rate of polymer from the downer to the riser. The flow rate between these two sections can be calculated as

$$F_p^r = \frac{C_{max}^r}{\tau^r} = \frac{C_{max}^r}{u_s^r L^r} \tag{12}$$

$$C_{max}^r = V^r \rho_p (1 - \varepsilon^r) \tag{13}$$

Catalyst or prepolymerized particles are also continuously fed into the reactor to maintain constant the number of active sites in the reactor, because polymer is removed in the downer section. The simulation of the riser considers this make-up setting the initial condition in the simulation of the riser

$$R_0|_{z=0}^r = R_0|_{z=L}^d + q \tag{14}$$

The downer section modeling is based on the packed-flow model presented by Kunii and Levenspiel.[4] This model assumes that the gas and solids flow downward at different but very close velocities. The equations for gas concentration, temperature, active sites concentration, and polymer moments are almost identical to the equations for the riser [eqs. (1), (2), (5)-(11)] but the porosity in those equations must

be changed to the porosity of the bed in the downer (ε^d).

The velocity of the solids in the downer is controlled by the value at the bottom of the section, which transfer solids to the riser. The solids velocity is calculated as to maintain constant the flow rate of solids in the riser and in the downer, so no accumulation of solids will occur in either section

$$F_p^d = F_p^r \tag{15}$$

$$u_s^d = \frac{L^d}{\tau^d} = \frac{L^d}{C_{max}^d} F_p^d \tag{16}$$

The moments of the polymer consider the effects of the formation or initiation of active sites, propagation, and transfer to monomer and chain transfer agent (CTA). Table I presents the kinetic model parameters for ethylene polymerization by Ziegler–Natta catalyst.[7]

RESULTS

Several simulations were made to explore the operating possibilities of the MZC reactor and to understand the behavior of the reactor and the polymer properties
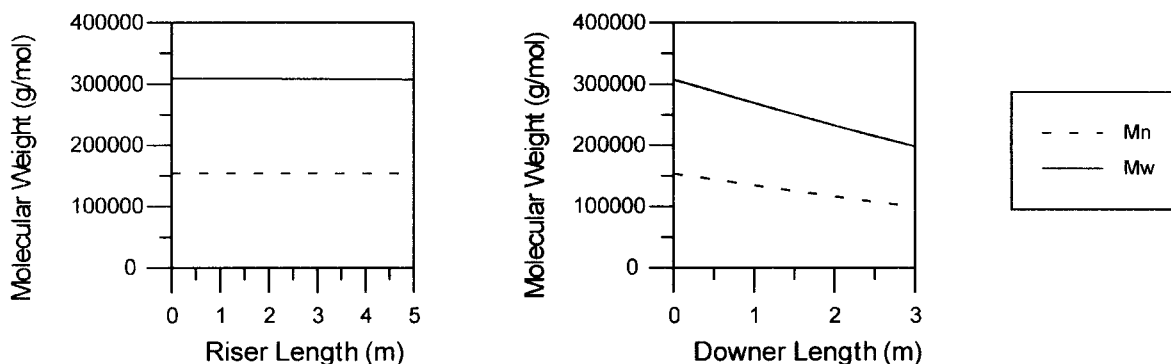

Figure 4 Instantaneous weight-average molecular weight being produced in the reactor as functions of the height of the riser and downer sections.
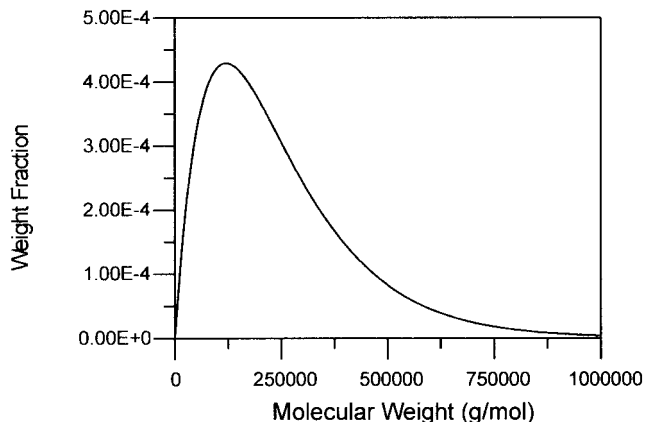
Figure 5 Cumulative molecular weight distribution of the polymer.

derived from each operating condition. The simulations were carried out with the reactor operating without gas barrier in the downer section. The simulations of the reactor operating with gas barrier are detailed in Part II of this article.

When operating without gas barrier, the gas concentration at the top of the downer section is the same as the conditions at the end of the riser section. The porosity of the bed, solid velocity, and gas velocity, however, will differ. Table II presents the operating conditions used in the simulations.

As typical behavior of the MZCR, there is a low consumption of gas in the riser due to the high bed porosity, reduced concentration of solids, and short residence time in this section. On the other hand, the consumption of gas in the downer is high due to the low bed porosity, long residence time of the solids, and greater amount of solids. Figure 3 shows the concentration of gas throughout the reactor.

The operating conditions and fluodynamics of the MZCR leads to a reduction of the monomer/hydrogen ratio throughout the downer because the monomer is rapidly consumed but hydrogen concentration changes only slightly, maintaining almost the same level throughout the entire section. Because the concentration of hydrogen is constant and the concentration of monomers decreases continuously, polymers with different molecular weights will be produced throughout the downer (Fig. 4).

These different molecular weights that are produced will lead to a polymer with broader molecular weight distribution that can be desired for some applications. Unlike a polymer blend where each particle in the blend has its own molecular weight, the polymer produced by the MZCR has several molecular weights in the same particle and, hence, the homogeneity of the polymer mixture is improved. Figure 5 shows the cumulative molecular weight distribution for a polyethylene produced under the conditions presented in Table II.

Figure 6 shows the instantaneous molecular weight distributions produced in each part of the reactor. As can be seen, there is a significant difference among them that helps in broadening the final molecular weight distribution.

It must be stated that the production of polymers with different molecular weights in a single particle is exclusive to the MZCR. Conventional fluidized bed reactors can produce only one kind of molecular weight with relatively narrow distribution, and this characteristic is emphasized even more when metallocenes are used. In FBRs, the broadening of the molecular weight distribution can be attained by the use of mixtures of different Ziegler–Natta catalysts, with each catalyst being prepared so as to give a different response to hydrogen. Although a mixture of granules
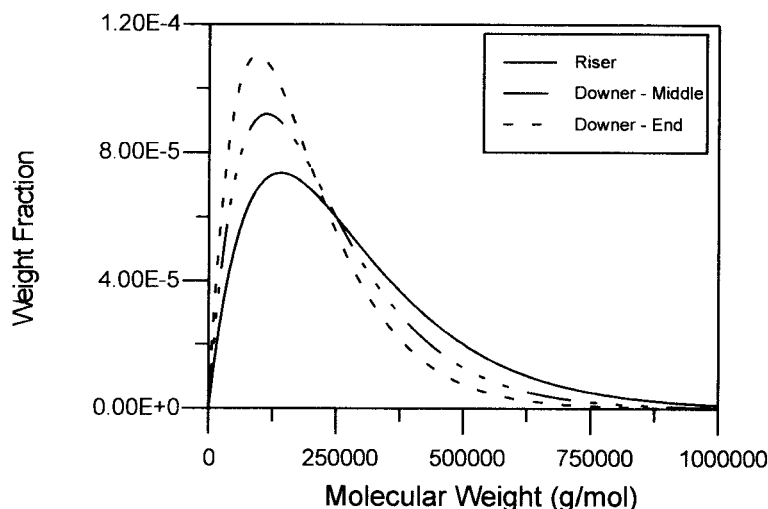

Figure 6 Instantaneous molecular weight distribution of the polymer at different parts of the reactor.
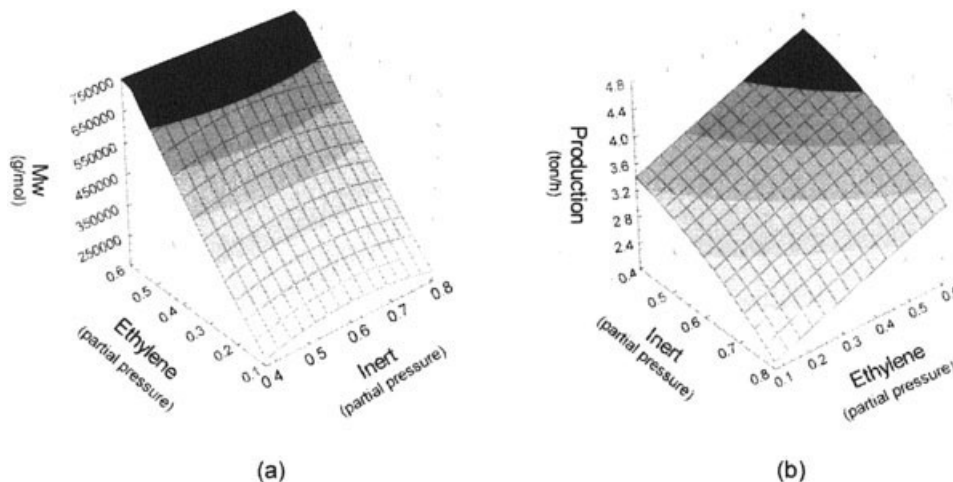
Figure 7   (a) Weight-average molecular weight (M_w) as a function of the partial pressures of ethylene and inert present in the gas feed; (b) Productivity as a function of the partial pressures of ethylene and inert present in the gas feed.

with different molecular weights is obtained at the exit from the reactor, the homogeneity of the product is still not satisfactory.

Effect of inert concentration

One or more inert gases can be maintained in the polymerization zones, in such quantities that the sum of the partial pressure of inert gases is between 5 and 80% of the total pressure of the gases. The inert gases can be nitrogen or an aliphatic hydrocarbon having from two to six carbon atoms.[2] The presence of inert gases makes it possible to limit the reaction rate, helps to maintain the partial pressure, and removes part of the heat generated by the reaction.

Figure 7(a) shows how the molecular weight of the polymer changes as a function of the concentration of

ethylene and inert of the reaction mixture (same conditions as presented in Table II). Figure 7(b) shows how the productivity of the reactor is affected by the concentration of inert and monomer, showing that it is possible to optimize the productivity of the reactor based on the gas mixture fed into the reactor, decreasing the amount of inert present in the gas mixture. The ratio of monomers/inert should not increase too much the temperature in the downer (increase above the polymer melt temperature), otherwise the polymer could melt and stick to the reactor wall, leading to the need to shut down the reactor.

Effect of catalyst flow rate

The reactor can be operated at different catalyst flow rates to establish different quantities of active sites
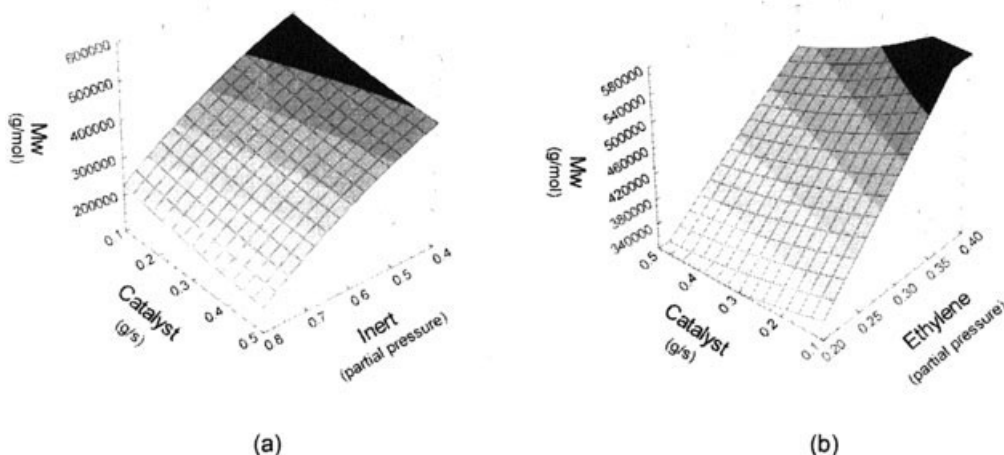

Figure 8   Weight-average molecular weight (M_w) of the polymer as function of the catalyst flow rate and the partial pressures of inert (a) and ethylene (b). (a) Ethylene/butene ratio at 1.7; (b) inert partial pressure at 0.6.
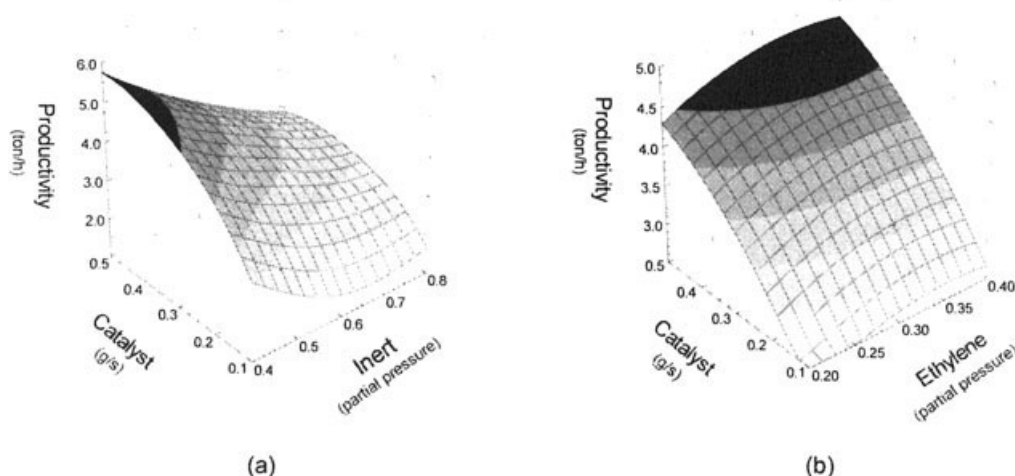
Figure 9 Productivity of the reactor as a function of the catalyst flow rate and the partial pressures of inert (a) and ethylene (b). (a) Ethylene/butene ratio at 1.7; (b) inert partial pressure at 0.6.

reacting in the reactor at one time. Catalyst flow rates of 0.10 to 0.50 g/s were simulated.

As shown in Figure 8, a greater flow rate will lower the average molecular weight of the polymer being produced, because a greater amount of active sites will compete for the available monomer. Increasing the amount of inert will also lower the molecular weight because the polymerization rate will diminish.

The catalyst flow rate has a positive influence on the productivity of the reactor, because higher flow rates imply more chains are propagating. Inert concentration limits the productivity by reducing the monomer concentration in the reactor, whereas an increase in the ethylene partial pressure will enhance the productivity because of its higher reactivity in relation to 1-butene (comonomer) (Fig. 9).

High-catalyst flow rates sometimes can reflect in a very high monomer consumption, which diminishes greatly the concentration of monomers along the

downer (Fig. 10). Consequently, there will be production of a large range of molecular weights throughout the downer (Fig. 11), leading to a polymer with high polydispersity, which may or may not be desirable for a given polymer (depending on its application). If a narrow polydispersity is desired for this system, it is possible to add more monomer at an intermediate point along the downer, increasing the concentration of monomers.

Effect of the gas velocity in the riser

The velocity of the gas in the riser will affect the residence time in the reactor, in both the riser and the downer sections. Velocities between 5 and 15 m/s were simulated in the riser. Other operating conditions remained as shown in Table II.

Setting a higher gas velocity in the riser will increase the particle velocity in the riser and thus will transfer
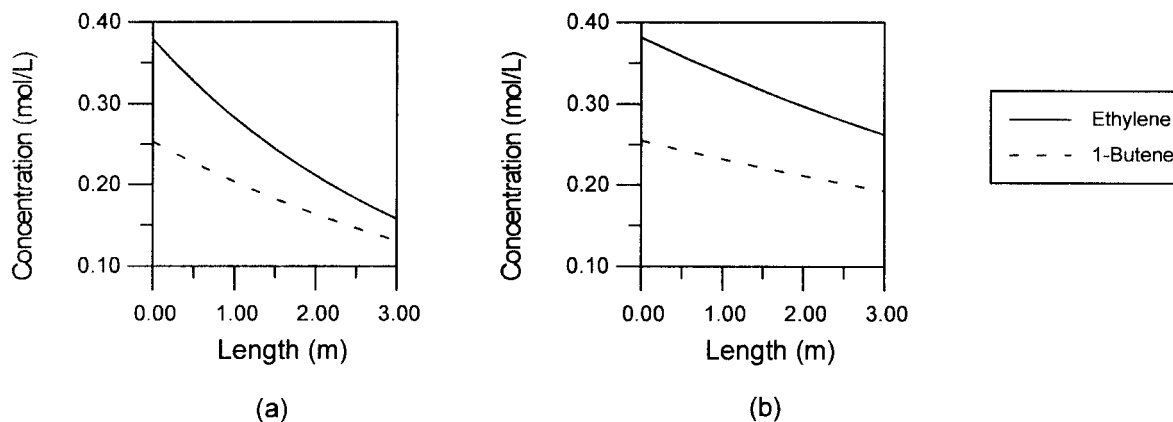

Figure 10 Concentration of the monomers in the downer for catalyst flow rates of 0.50 g/s (a) and 0.10 g/s (b). Other operating conditions as shown in Table II.
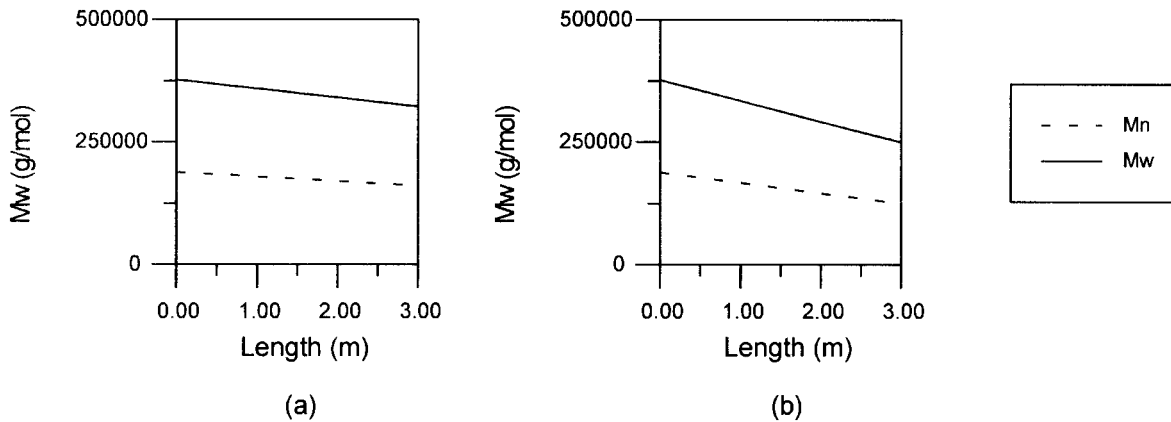
Figure 11 Instantaneous molecular weights at the downer for catalyst flow rates of 0.50 g/s (a) and 0.10 g/s (b). Other operating conditions as shown in Table II.

more particles to the downer section that, to maintain a steady bed weight, will also need to transfer more particles to the riser, increasing the particles velocity in the downer and decreasing the residence time in the section. The higher velocity in the sections will reflect in lower gas consumption per pass in both sections (Fig. 12). The molecular weight of the polymer will be slightly affected by the lower decrease in the gas concentration along the reactor and the molecular weight will tend to remain almost constant throughout the reactor, or will have a slight reduction in its molecular weight (Fig. 13).

As a consequence, the gas velocity in the riser will not have great influence on the molecular weight of
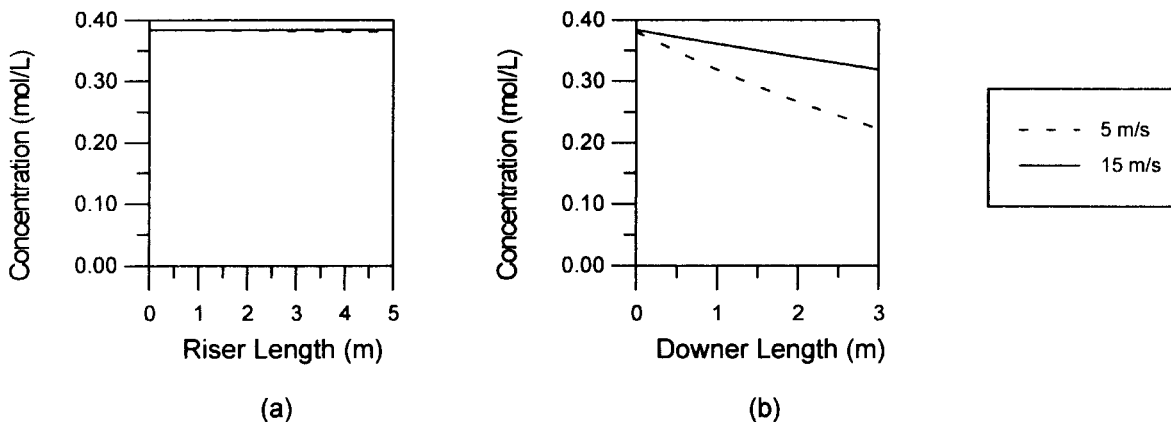

Figure 12 Concentration of monomers in the reactor for gas velocities in the riser of 5 and 15 m/s.
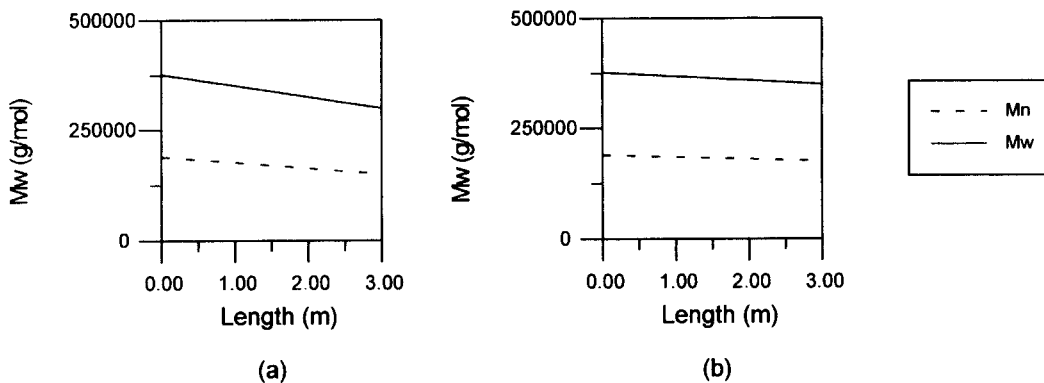

Figure 13 Instantaneous molecular weights in the downer for gas velocities in the riser of 5 m/s (a) and 15 m/s (b).
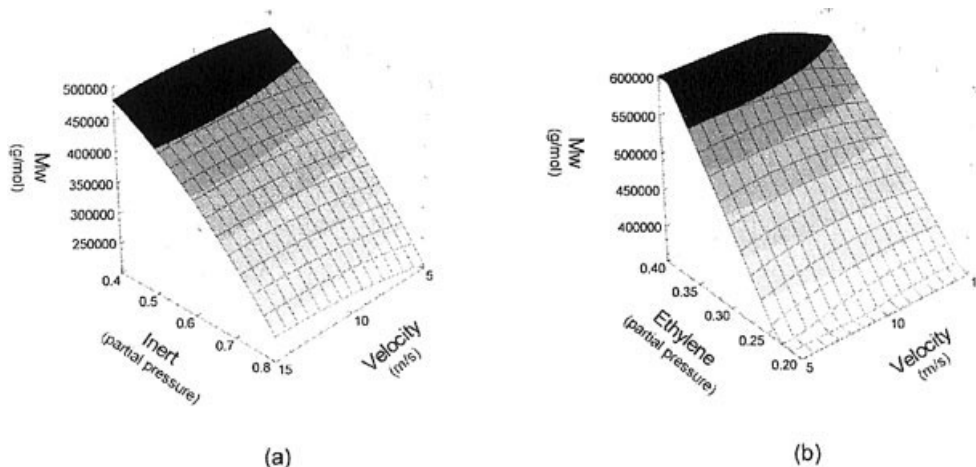
Figure 14 Weight-average molecular weight (M_w) of the polymer as function of the gas velocity in the riser and the partial pressures of inert (a) and ethylene (b). (a) Ethylene/butene ratio at 1.7; (b) inert partial pressure at 0.6.

the polymer (Fig. 14). The productivity of the system will increase satisfactorily when higher gas velocities are used in the riser. This happens because the concentration of monomers is maintained at high levels in the entire reactor, leading to higher reaction rates and production (Fig. 15).

Effect of the porosity in the riser

The porosity in the riser can be controlled by feeding more or less catalyst from the downer to the riser, which will change the amount of particles in the riser and thus the porosity. It should be stated that porosities between 0.80 and 0.99 are needed to maintain the conditions for pneumatic transport in the riser. Setting the porosity in the riser will set the load of polymer

and active site concentration in the riser, thus resulting in a higher or lower monomer consumption.

A decrease in the porosity in the riser will lead to a higher consumption of monomers in the riser but this increase will be slight: less than 3% for the smallest porosity (0.85), compared to the higher porosity (0.95). The effect in the downer is the opposite, and a decrease in the riser porosity will lead to a decrease in the overall consumption of monomers in the downer because the residence time in the downer will be reduced (Fig. 16).

The effects of changing the porosity in the reactor on the molecular weight of the polymer and productivity are similar to the effects of changing the velocity in the riser. Increasing the porosity in the riser will allow the polymer to have a slightly higher fraction of chains
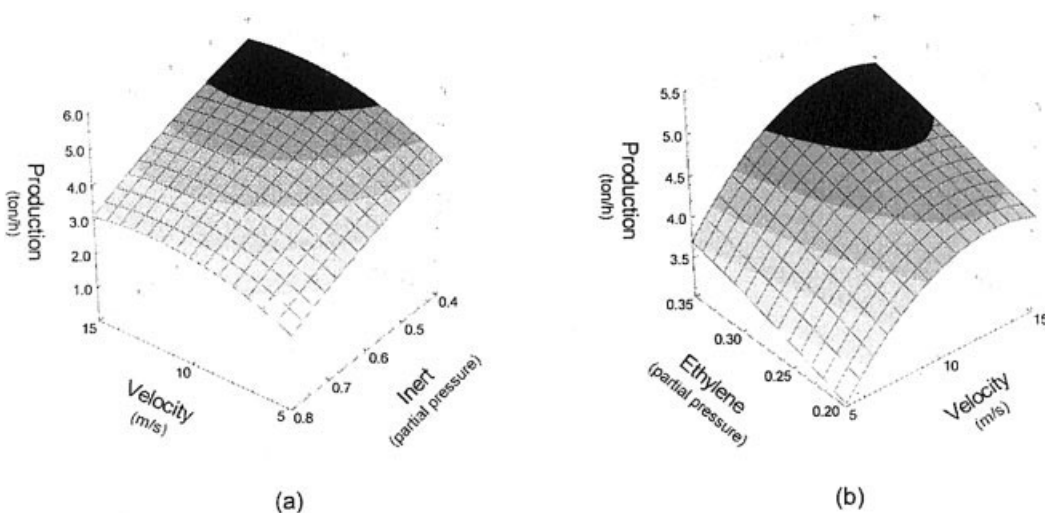

Figure 15 Productivity of the reactor as function of the gas velocity in the riser and the partial pressures of inert (a) and ethylene (b). (a) Ethylene/butene ratio at 1.7; (b) inert partial pressure at 0.6.
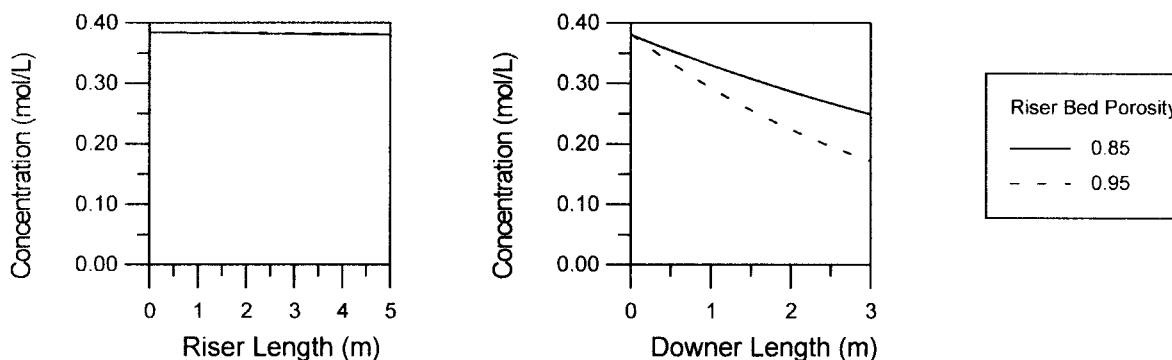
Figure 16   Concentration of monomer (ethylene) in the reactor for porosities of 0.85 and 0.95 m.

produced in the riser, which does not occur when increasing the velocity in the riser (in both cases the residence time in the downer is reduced).

Effect of the downer bed height

The downer bed height will directly affect the residence time in this section. The particles flow rate to the riser is maintained at a constant level, but the amount of solids will change, and consequently, the residence time will also change. Downer bed heights of 2.5 to 4.5

were simulated for the operating conditions presented in Table II. The effect of downer bed height is shown in Figures 17 and 18.

Smaller bed heights will allow a higher solid circulation among the sections of the reactor, increasing the importance of the riser section, because the circulation between the two sections will be higher. The downer bed height does not have a pronounced effect on the molecular weight of the polymer as can be observed in Figure 18, where the molecular weight remains practically constant over the entire reactor. The bed height
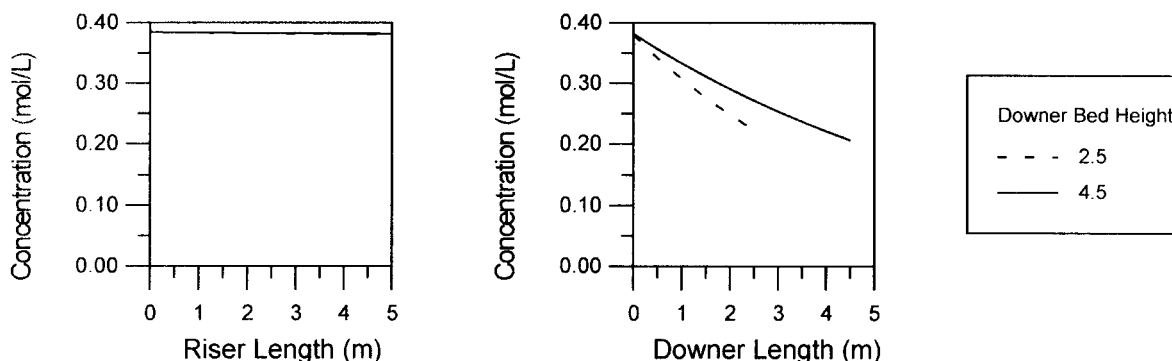

Figure 17   Concentration of monomer (ethylene) in the reactor for downer bed height of 2.5 and 4.5 m.
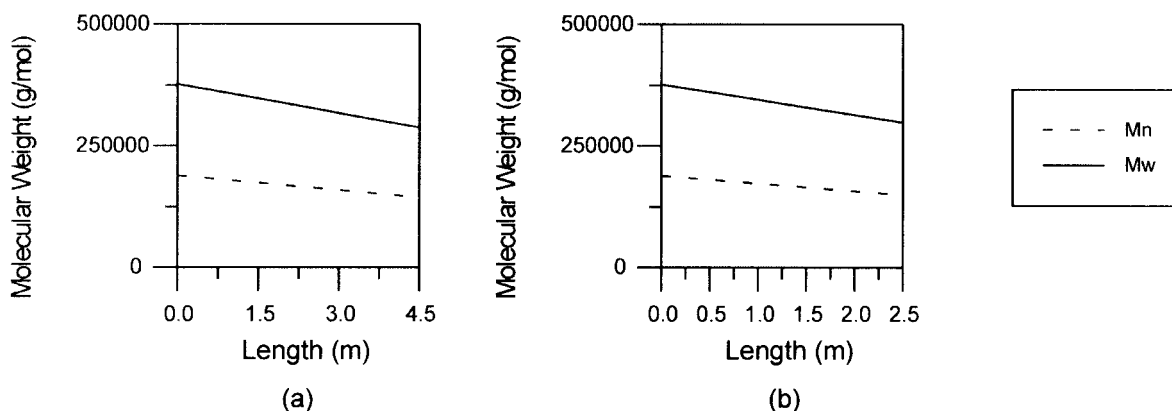

Figure 18   Molecular weights of the polymer in the downer for downer bed height of 4.5 (a) and 2.5 m (b).
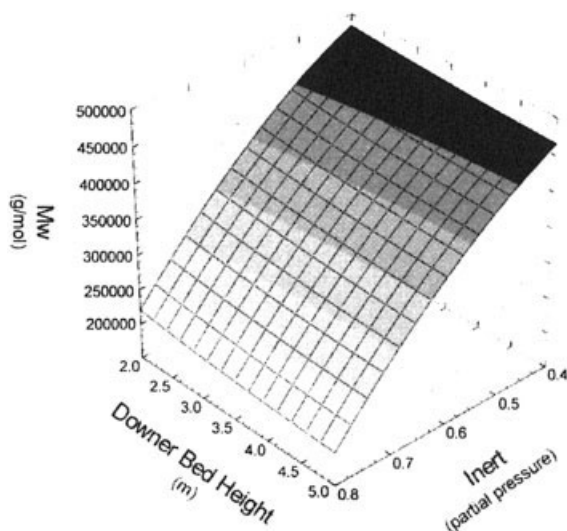
Figure 19 Weight-average molecular weight of polyethylene as function of the downer bed height and inert partial pressures (ethylene/butene ratio of 1.7).

has a huge effect on the reactor productivity, because smaller bed heights lead to higher solids circulation and, hence, the polymer will spend more time under conditions where the concentration of monomers is higher, enhancing the productivity because of a higher reaction rate throughout the reactor (Fig. 19).

CONCLUSION

The development of a mathematical model for the multilane circulating reactor was done, and simulations showed that the reactor is capable of producing different molecular weights inside a single polymer particle. The molecular weight distribution and its width (polydispersity) can be controlled by setting different operating conditions, such as catalyst flow rate, partial pressure of monomer and inert, gas velocity in the riser, porosity in the riser, and bed height in the downer. The number of operating conditions that can be set and changed is higher than in conventional fluidized bed reactors; thus, the MCZR gains also in flexibility. In Part II of this article, the effects of a gas barrier in the downer are addressed.

NOMENCLATURE

C_i concentration of gas i
C_{max} maximum load of solids
Cp molar heat capacity
$Cp*$ mass heat capacity
F_p solids flow rate
H_2 hydrogen concentration

kf formation of active sites rate constant
kfm transfer to monomer rate constant
kfh transfer to hydrogen rate constant
ki initiation of active sites rate constant
kp propagation rate constant
L length
q catalyst flow rate
Q_i moment i of the dead polymer
$R*$ concentration of active sites
R_0 concentration of potential active sites
Rp reaction rate
T temperature
u velocity
u_0 gas superficial velocity
u_{slip} relative velocity between gas and solids
V volume
Y_i moment i of the live polymer
z length

Greek letters

ε porosity
τ residence time
ρ density

Subscripts

g gas
p polymer
s solids
t terminal

Superscripts

d downer
r riser

References

1. Covezzi, M.; Mei, G. Chem Eng Sci 2001, 56, 4059.
2. Govoni, G.; Rinaldi, R.; Covezzi, M.; Galli, P. WO Pat. 2,200,428, 1997.
3. Govoni, G.; Covezzi, M. WO Pat. 2,301,517, 2000.
4. Kunii, D.; Levenspiel, O. Fluidization Engineering; Butterworth-Heinemann: New York, 1991.
5. Geldart, D. Gas Fluidization Technology; Wiley: New York, 1986.
6. Galli, P.; Vecellio, G. Prog Polym Sci 2001, 26, 1287.
7. McAuley, K. B.; MacGregor, J. F.; Hamielec, A. E. AIChE J 1990, 36, 837.