Multizone Circulating Reactor Modeling for Gas-Phase Polymerization. II. Reactor Operating with Gas Barrier in the Downer Section

Fabiano A. N. Fernandes,[1] **Liliane M. F. Lona**[2]

[1]*Universidade Federal do Rio Grande do Norte, Departamento de Engenharia Química, Av. Senador Salgado Filho 3000, 59072-970 Natal–RN, Brazil*
[2]*Universidade Estadual de Campinas, Faculdade de Engenharia Química, Departamento de Processos Químicos, Caixa Postal 6066, 13083-970 Campinas–SP, Brazil*

Received 30 October 2003; accepted 24 February 2004
DOI 10.1002/app.20572
Published online in Wiley InterScience (www.interscience.wiley.com).

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 multizone 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. In the first part, we presented a mathematical model for the reactor, and this second part of the article we present simulations when a gas barrier is introduced in the top of the downer section and its implications in the polymer characteristics. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1053–1059, 2004

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

INTRODUCTION

New reactor technologies were developed to expand the properties for polyolefins resins, by conducting polymerization in two or more polymerization steps, each of them under different operating conditions and producing polymers with different molecular weight and composition. One of the promising new reactor technologies is the multizone circulating reactor (MZCR) that is being developed by Bassell (Hoofdorp, The Netherlands). The advantage of the MZCR is the possibility of applying two different operating conditions in the reactor (one in the riser section and one in the downer section), making the polymer circulate continuously between the two sections. This feature will produce a polymer particle with an onion ring structure where the rings alternate polymer produced in the riser with polymer produced in the downer. A mathematical model for the multizone circulating reactor was presented in Part I of this series of articles[1] and this part will deal with the use of a gas barrier in the downer section. A parameter sensitivity analysis will also be shown to present how each operating and design parameter can change the reactor behavior and polymer characteristic.

Correspondence to: F. A. N. Fernandes (fabiano@efftech.eng.br).
Contract grant sponsor: Fundação de Amparo à Pesquisa do Estado de São Paulo.

Journal of Applied Polymer Science, Vol. 93, 1053–1059 (2004)

MULTIZONE CIRCULATING REACTOR

The concepts for the MZCR and some partial data were reported by Covezzi and Mei,[2] Govoni et al.,[3] and Govoni and Covezzi.[4] The reactor configuration provides the polymerization in gas phase in two polymerization zones made by two cylindrical interconnected vertical legs (riser and downer) in which the polymer is circulating continuously. The MZCR can be operated with a gas barrier in the downer section, and in this case, an additional gas feed is made in the top of the downer section (Fig. 1).

The two different operating conditions, in the downer and in the riser, can be attained by preventing the gas from the riser from entering the downer section and by feeding a different gas mixture in the downer. This can be achieved by feeding a gas and/or liquid into the downer. The gas mixture to be fed into the downer should have an appropriate composition, different from that of the riser. This gas mixture partially or totally replaces the gas mixture entrained within the polymer particles entering the downer. The flow rate of the feed can be regulated so that a flow of gas countercurrent to the flow of the polymer particles is developed in the downer section, thus acting as a barrier to the gas mixture coming from the riser, which is entrained among the polymer particles.[4]

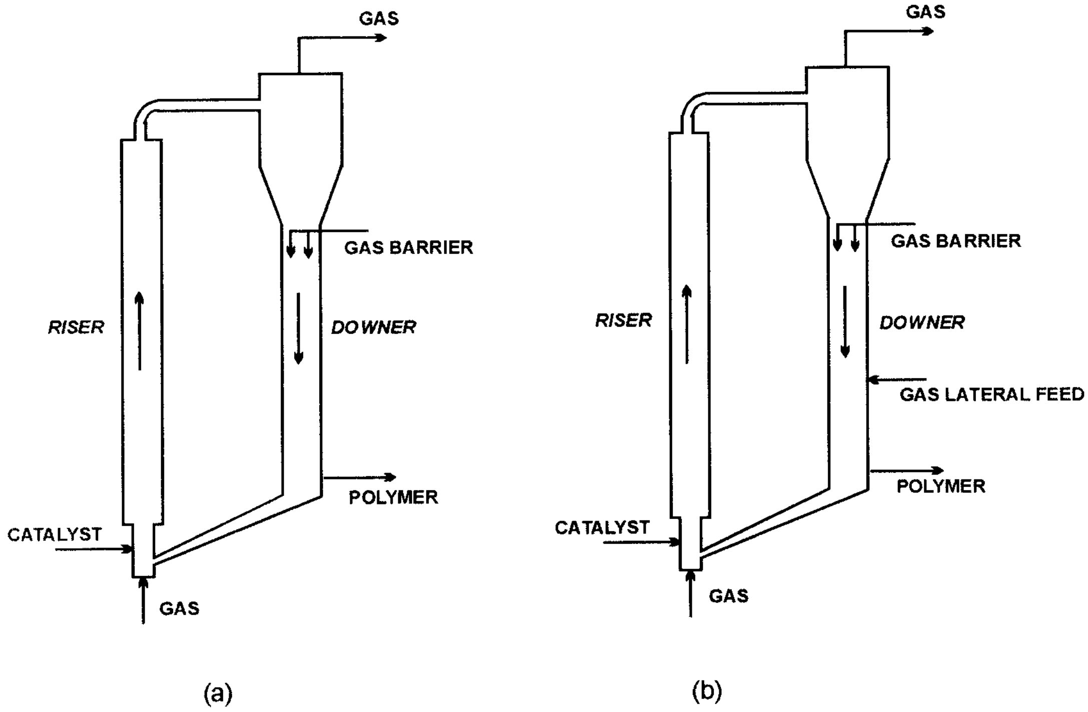

Figure 1 Multizone circulating reactor diagram with introduction of a gas barrier at the top of the downer section. (a) Reactor with gas barrier. (b) Reactor with gas barrier and lateral feed.

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 in 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[5] and the downer section modeling is based in the packed-flow model also presented by Kunii and Levenspiel.[5] The moments of the polymer considers the effects of the formation or initiation of active sites, propagation, and transfer to monomer and chain transfer agent (CTA).

The mathematical equations and modeling assumptions were described in detail in Fernandes and Lona.[1] The only difference concerns the initial conditions in the downer section. When operating without a gas barrier in the downer, the initial conditions (gas concentration, polymer moments, and temperature) to simulate the downer are the results (or final conditions) of the riser section. When operating with a gas barrier, the initial conditions in the downer section are

TABLE I
Initial Conditions for the Simulation of Downer Section of the MZCR

	Without gas barrier	With gas barrier
Gas concentration	$C_i^d \mid_0 = C_i^r \mid_L$	$C_i^d \mid_0 = C_i^{gb}$
Temperature	$T^d \mid_0 = T^r \mid_L$	$T^d \mid_0 = T^{gb}$
Polymer moments	$Y^d \mid_0 = Y^r \mid_L$	$Y^d \mid_0 = Y^r \mid_L$
	$Q^d \mid_0 = Q^r \mid_L$	$Q^d \mid_0 = Q^r \mid_L$

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 in the riser	5.0 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 flow rate	0.50 g/s
Downer	
Height	3.0 m
Diameter	0.3 m
Gas velocity in the downer	0.4 m/s
Porosity	0.15
Operating condition A	
Ethylene concentration	0.192 mol/L
1-Butene concentration	0.021 mol/L
Inert concentration (nitrogen)	0.854 mol/L
Hydrogen concentration (CTA)	0.010 mol/L
Operating condition B	
Ethylene concentration	0.576 mol/L
1-Butene concentration	0.064 mol/L
Inert concentration (nitrogen)	0.427 mol/L
Hydrogen concentration (CTA)	0.010 mol/L

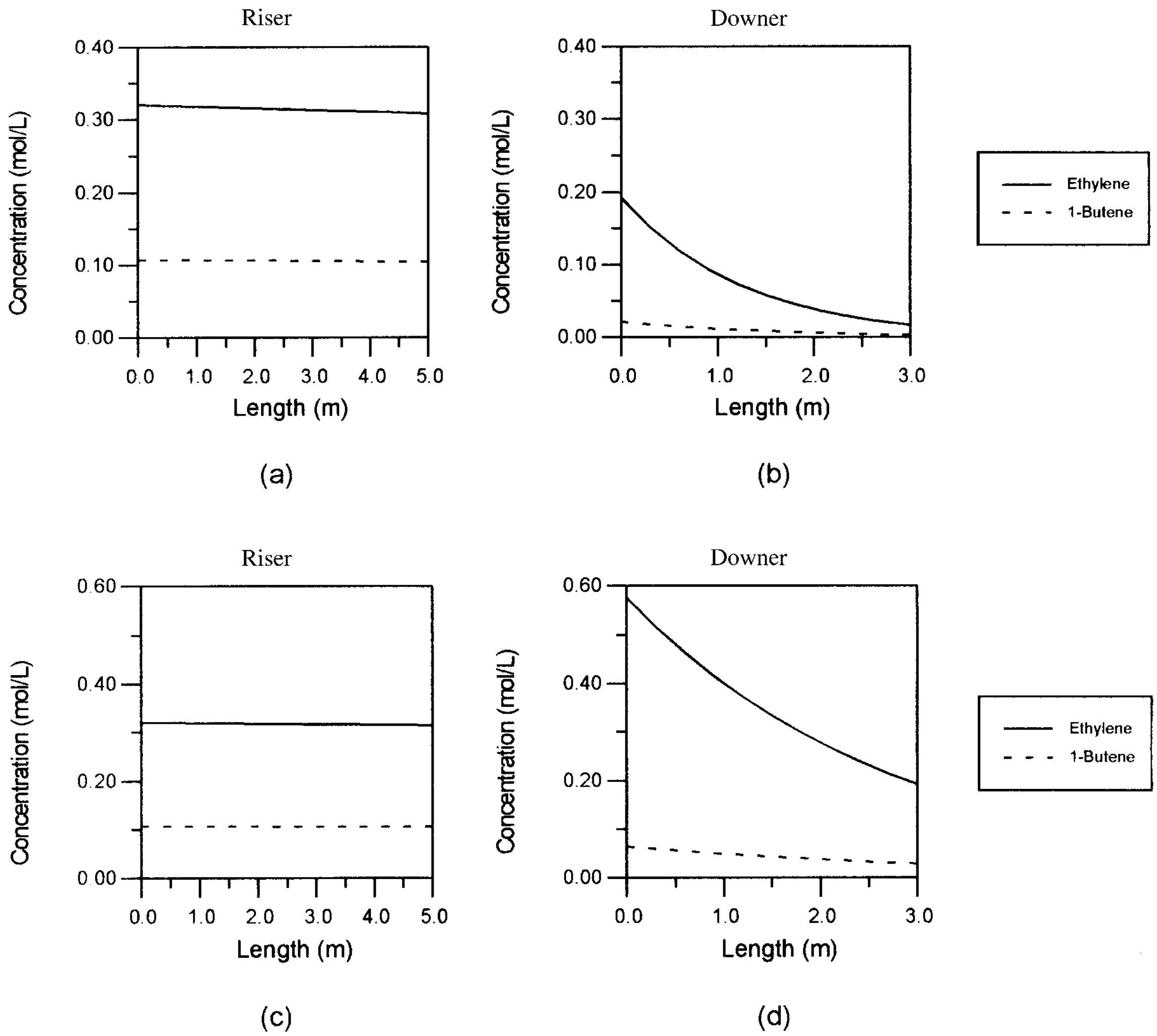

Figure 2 Concentration of monomers throughout the riser and downer sections. Operating condition A (a, b). Operating condition B (c, d).

the new gas concentration and the temperature set by the gas barrier, while the initial condition for the polymer moments is the condition of the polymer moments at the end of the riser (Table I).

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 derived from each operating condition, when using a gas barrier in the downer section. Two operating conditions in the downer section are shown for comparative purposes in this article. The operating conditions A and B in the downer are shown in Table II. Riser conditions remained the same throughout the simulations.

The operation of the reactor with the gas barrier presents a concentration profile similar to the operation of the reactor without the gas barrier. The concentration throughout the riser tends to remain constant and a more accentuated consumption of monomer occurs in the downer. Depending on the operating conditions, the consumption in the downer will be higher or lower. Figure 2 shows the concentration profiles for the operating conditions A and B (Table II).

In relation to the instantaneous molecular weights being produced throughout the reactor, when an operating condition that produces a lower molecular weight is used in the downer, the molecular weight will diminish continuously, following the decrease in the monomer concentration. However, when an operating condition that produces a higher molecular weight is used in the downer, the molecular weight will increase rapidly and then will decrease at a lower rate if compared to the latter case (Fig. 3).

For the operating condition A, the cumulative molecular weight distribution will be highly affected by

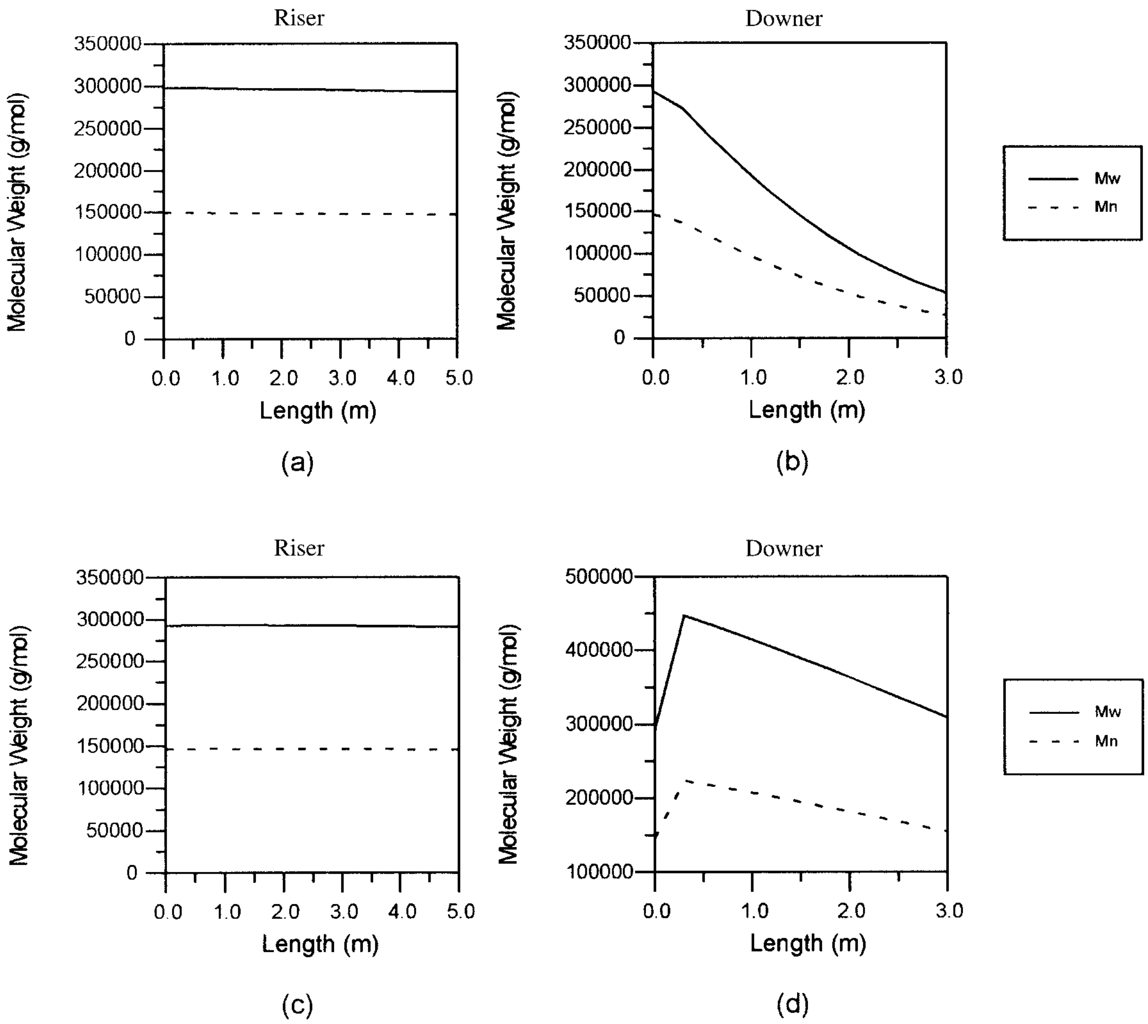

Figure 3 Instantaneous weight-average molecular weight being produced in the reactor as a function of the height of the riser and downer sections. Operating condition A (a, b). Operating condition B (c, d).

the production of polymer with low molecular weight in the downer and few chains with high molecular weight will be produced (Fig. 4). In this case, there is a big difference between the polymer produced in the riser and in the downer, where the riser will produce chains with high molecular weight and the downer will produce many chains with low molecular weight, affecting the polydispersity of the resin (Fig. 5).

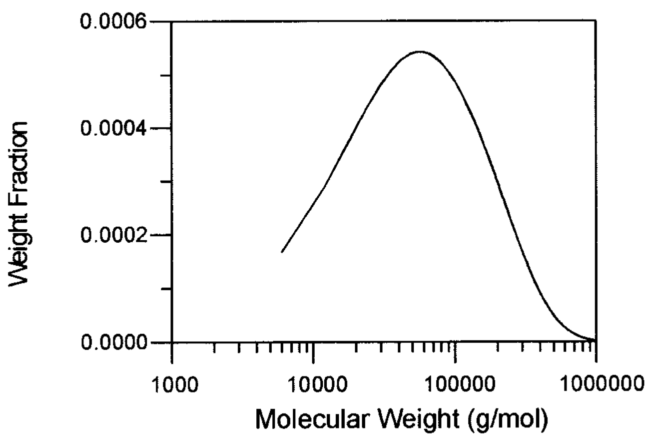

Figure 4 Cumulative molecular weight distribution for operating condition A.

For the operating condition B, the molecular weight distribution will be affected by the polymer of high molecular weight produced in the riser and in the downer (Fig. 6). In this case, there is a slight difference between the polymer from the riser and from the downer, and thus, the polydispersity of the polymer will not be highly modified (Fig. 7).

Effect of the gas velocity in the riser

An increase in the gas velocity in the riser will increase the solids velocity in the riser as well, leading to an increase in the amount of solids flowing through the riser per unit of time. As a result, there will be an increase in the velocity of solids in the downer to match the flow rate between downer and riser and *vice*

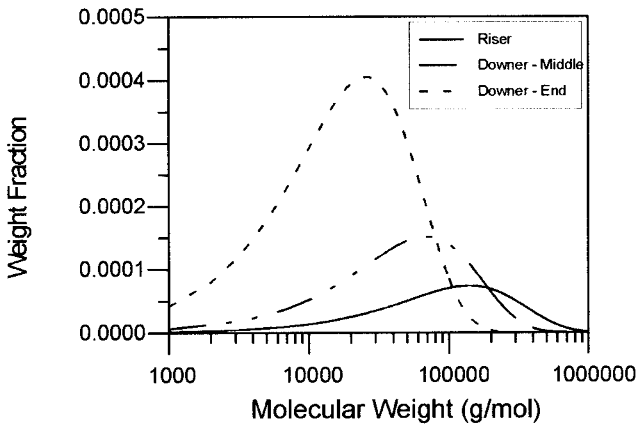

Figure 5 Instantaneous molecular weight distributions for operating condition A at the riser, at the middle of the downer, and at the end of the downer.

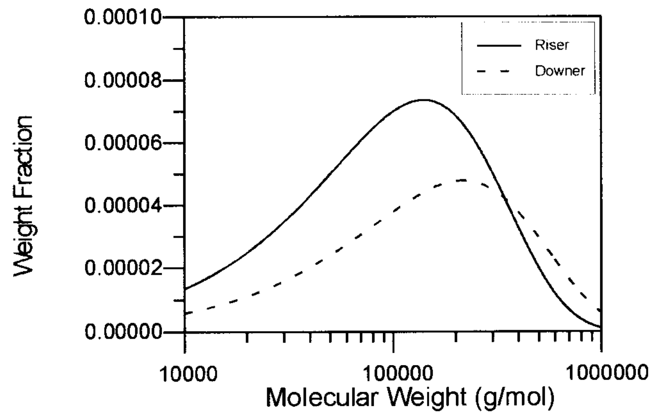

Figure 7 Instantaneous molecular weight distributions for operating condition B at the riser and at the end of the downer.

versa. Thus, the overall solids circulation time in the reactor will decrease, affecting the residence time in both the riser and the downer sections. Velocities between 5 and 15 m/s in the riser were simulated.

The lower residence time in both sections will reduce the consumption of monomers in the sections, leading to a lower decrease of monomer concentration in the downer and constant concentration in the riser. Figure 8 shows a comparison of ethylene concentration in the downer for gas velocities in the riser of 5 and 15 m/s, for operating conditions A and B.

The lower gas consumption will imply production of polymer chains with molecular weight not much different throughout the reactor (Fig. 9).

A lower gas velocity in the riser will lead to a broader molecular weight distribution with production of more low molecular weight product in the downer section, whereas a higher gas velocity in the riser will lead to a narrower molecular weight distribution with a greater amount of polymer with high

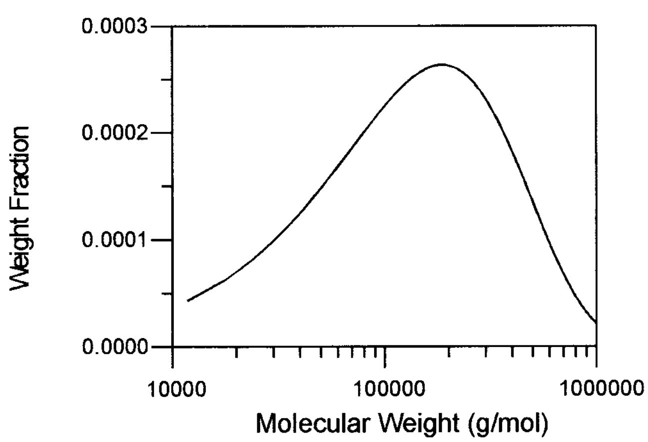

Figure 6 Cumulative molecular weight distribution for operating condition B.

molecular weight (Figs. 10 and 11). Although a lower gas velocity in the riser will increase the influence of the polymer produced in the riser on the overall molecular weight distribution of the final polymer, this increase is rather small if compared to the increase of low molecular weight product caused by the higher residence time in the downer section.

Effect of the downer bed height

The bed height of the downer can be controlled and will affect the residence time of the polymer in the downer. As a consequence, the concentration of monomers in the downer will remain at high levels when smaller bed heights are used. This will boost productivity because of higher polymerization rates throughout the downer and will lead to a slightly narrower molecular weight distribution because the monomer/hydrogen ratio will change only slightly. Figures 12 and 13 show the molecular weight distributions for operating conditions A and B, respectively. The figures show that a smaller bed height will produce polymers with slightly higher molecular weights.

Effect of the porosity in the riser

The porosity in the riser affects the amount of polymer present in the section and thus the circulation time in the reactor (Fig. 14, condition A; Fig. 15, condition B). A decrease in the riser porosity increases the amount of polymer in this section and diminishes the residence time in the downer, because more polymer has to be transferred to the riser. The residence time in the riser does not change.

Changing the porosity will affect only slightly the reactant consumption in the riser, but a decrease in the riser porosity will decrease the consumption of mono-

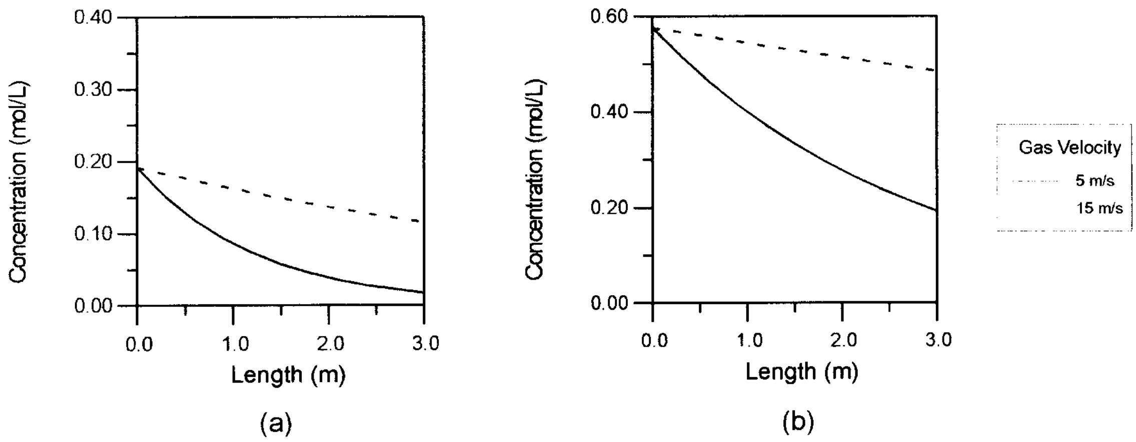

Figure 8 Ethylene concentration throughout the downer for gas velocities in the riser of 5 and 15 m/s, for operating conditions A (a) and B (b).

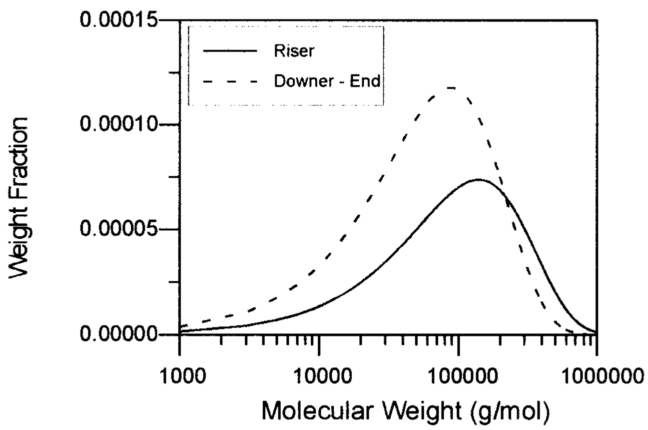

Figure 9 Molecular weight distribution for operating condition A and gas velocity in the riser of 15 m/s, at the riser, and at the end of the downer.

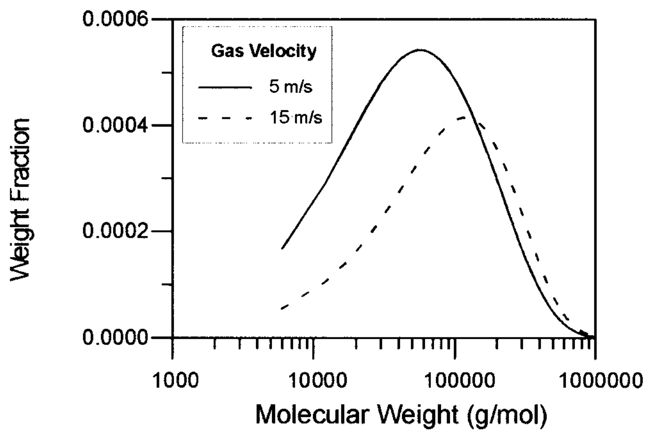

Figure 10 Cumulative molecular weight distribution for operating condition A and gas velocity in the riser of 5 and 15 m/s.

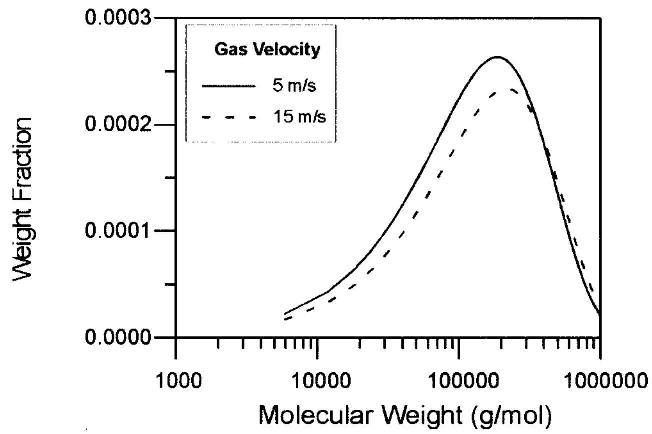

Figure 11 Cumulative molecular weight distribution for operating condition B and gas velocity in the riser of 5 and 15 m/s.

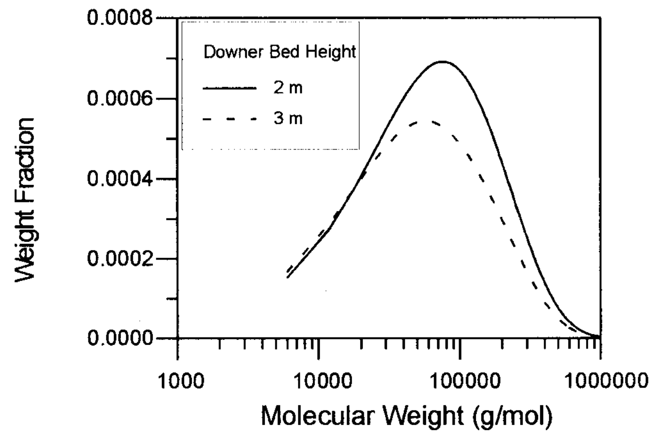

Figure 12 Molecular weight distribution for operating condition A and downer bed heights of 2 and 3 m.

mers in the downer because the residence time in this section will also decrease. As a consequence, the polymer produced in the riser will have a higher influence on the overall molecular weight distribution of the final polymer. The influence of the polymer produced in the riser in this case is greater than when changing the gas velocity in the riser.

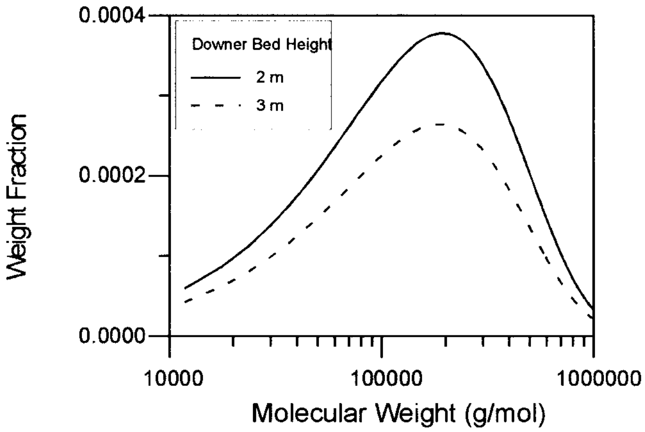

Figure 13 Molecular weight distribution for operating condition B and downer bed heights of 2 and 3 m.

CONCLUSION

Part I of this article showed the development of a mathematical model for the multizone circulating reactor and presented several simulations to infer that the reactor is really capable of producing different molecular weights inside a single polymer particle. In this second part, we have shown how the behavior of the reactor changes when a gas barrier is introduced in the downer section.

The molecular weight distribution can be controlled by setting different operating conditions, such as the gas velocity in the riser, porosity in the riser, and bed height in the downer, and from different concentrations fed into the riser and downer. A study was conducted to verify how the operating conditions could produce a broader or narrower molecular weight distribution and how to increase or decrease the amount of polymers produced by the conditions applied in the downer and riser sections in the final polymer characteristics.

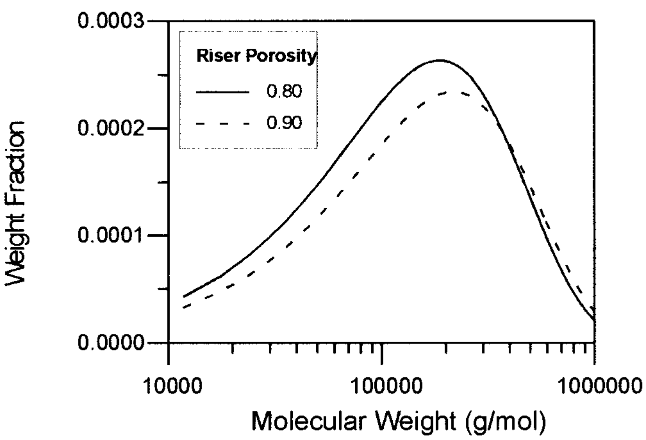

Figure 14 Molecular weight distribution for operating condition A and riser porosities of 0.80 and 0.90.

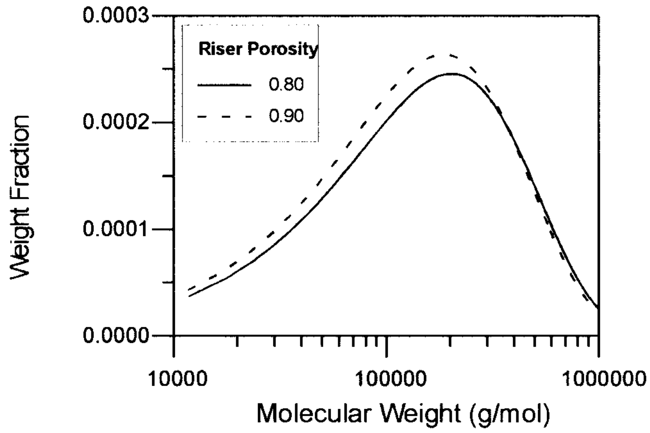

Figure 15 Molecular weight distribution for operating condition B and riser porosities of 0.80 and 0.90.

NOMENCLATURE

C_i concentration of gas *i*
L reactor length
Q_i moment *i* of the dead polymer
T temperature
Y_i moment *i* of the live polymer

Subscripts

0 initial condition
L condition at the end of the section

Superscripts

d downer
gb gas barrier
r riser

The authors gratefully acknowledge the financial support of the Brazilian research funding institution, Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

References

1. Fernandes, F. A. N.; Lona, L. M. F. J Appl Polym Sci to appear.
2. Covezzi, M.; Mei, G. Chem Eng Sci 2001, 56, 4059.
3. Govoni, G.; Rinaldi, R.; Covezzi, M.; Galli, P. WO Pat. 2,200,428, 1997.
4. Govoni, G.; Covezzi, M. WO Pat. 2,301,517, 2000.
5. Kunii, D.; Levenspiel, O. Fluidization Engineering; Butterworth-Heinemann: New York, 1991.