

MODELING AND SIMULATION OF A HIGH PRESSURE POLYETHYLENE TUBULAR REACTOR WITH AXIAL MIXING

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Abstract

The modeling and dynamic simulation of an ethylene polymerization reactor at high pressure was developed. During the dynamic modeling, it was considered a plug flow reactor with axial mixing, monophasic system, variations of the physical properties and overall heat transfer coefficient in the axial direction. The kinetic modeling included the oxygen initiation, propagation, termination by combination and by thermal degradation, chain transfer to the monomer, polymer and solvent, intramolecular transfer (backbiting) β -scission of secondary and tertiary radicals reactions. The reactor performance was analyzed by variations in the mixture degree through the temperature profiles and concentration.

1. Introduction

Developed in the decade of 1930, ethylene polymerization in high pressures is a reaction of great commercial interest. In view of that, it is natural that this process attracts the attention of a great number of researchers. The prediction of the reactor behavior, the determination of safe operation conditions and the process optimization are among the reasons that motivate its modeling.

An extensive review about modeling of LDPE process can be found in Zabisky *et al.* (1992). In general, the implemented models for this reactor do not consider diffusion, given the additional difficulty that this represents of the numeric point of view. However, the fact of industrial reactors use periodic pulsation to avoid polymer deposits justifies the concern in quantifying the effect of the diffusion in such systems.

Agrawal and Han (1975), using numbers of Peclet between 10 and 500, discovered that the axial mixing affects as much conversion as the quality of the product. Later, Yoon and Rhee (1985), using a relatively simple kinetic model, verified that the monomer conversion profiles for $Pe = 100$ and $Pe = \infty$ (no diffusion) exhibited great likeness. Arguing that the number of Peclet of this system is very superior to 100, the authors concluded that the axial dispersion can be neglected.

Preliminary studies, that did not consider diffusion, revealed us that the Reynold's number decreased drastically along the reactor, assuming very low values in the zone of larger concentration of polymer. This fact suggested us to investigate more deeply the effects of the axial mixing in the reactor profiles.

A jacket tubular polyethylene reactor, operating at pressures from 2000 to 3000 atm and temperatures between 150 and 350 °C is considered in this work. The objective is to verify the importance of the diffusion in the reactor performance, as well as to determine the thresholds from which the diffusive effects can be ignored.

2. Model Development

2.1 Kinetic model

The kinetic mechanism used in this work – that includes oxygen initiation, propagation, termination by combination and thermal degradation, transfer to monomer, polymer and

solvent, *backbiting* and β -scission of radicals – is described in Secchi and Bolsoni (1998), which is based on Brandolin *et al.* (1996). The kinetic constants are listed in Gupta *et al.* (1985). For simplicity, in the present modeling, the peroxide and third order monomer thermal initiations were not considered.

It was assumed that ethylene decomposition and termination by disproportionation can be neglected and the propagation reaction was adopted as the only thermally important step.

It was also supposed that the polymer size is a continuous variable and, therefore, the moments are given by (Saidel and Katz, 1968):

$$\lambda_{m,n} = \sum_i i^m \int x^n r_i(x) dx \quad (1)$$

$$\gamma_{m,n} = \sum_i i^m \int x^n p_i(x) dx \quad (2)$$

With these definitions, $\lambda_{0,0}$ and $\gamma_{0,0}$ represent the overall concentrations of free-radicals and polymer, respectively; $\lambda_{0,1}$ and $\gamma_{0,1}$ represent the monomer concentrations in the free-radicals and polymer; while $\lambda_{1,0}$ and $\gamma_{1,0}$ are the concentrations of long chain branching.

2.2 Reactor modeling

In the dynamic modeling of the tubular reactor, it was considered plug flow with axial diffusion, being the diffusivity evaluated through the variation of the number of Peclet. Besides, it was used the following hypotheses: homogeneous system and variations of the physical properties of the polymeric mixture (specific mass, viscosity and specific heat) and of the overall heat transfer coefficient in the axial direction.

From the overall mass balance, \dot{v} can be obtained that velocity derivative is given by the expression:

$$\left(\frac{\partial v}{\partial z} \right) = -\frac{v}{\rho} \left[\left(\frac{\partial \rho}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right) + \left(\frac{\partial \rho}{\partial P} \right) \left(\frac{\partial P}{\partial z} \right) + \left(\frac{\partial \rho}{\partial M} \right) \left(\frac{\partial M}{\partial z} \right) \right] \quad (3)$$

The reactor thermal balance is:

$$\rho \cdot c_p \left(\frac{\partial T}{\partial t} \right) = k \left(\frac{\partial^2 T}{\partial z^2} \right) - \rho \cdot c_p \cdot v \left(\frac{\partial T}{\partial z} \right) + (-\Delta H_r) k_p M \lambda_{0,0} - \frac{4 \cdot U}{D} (T - T_c) \quad (4)$$

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while the jacket thermal balance is given by:

$$\rho_w \cdot c_{pw} \left(\frac{\partial T_c}{\partial t} \right) = k_w \left(\frac{\partial^2 T_c}{\partial z^2} \right) - v_w \cdot \rho_w \cdot c_{pw} \left(\frac{\partial T_c}{\partial z} \right) - \frac{4 \cdot U}{D_{eq}} (T_c - T) \quad (5)$$

The mass balances of the several components can be written as:

- monomer:

$$\left(\frac{\partial M}{\partial t} \right) = D_m \cdot \left(\frac{\partial^2 M}{\partial z^2} \right) - v \cdot \left(\frac{\partial M}{\partial z} \right) - M \cdot \left(\frac{\partial v}{\partial z} \right) - (k_p M \lambda_{0,0} + k_o M O^\delta + k_{trm} M \lambda_{0,0}) \quad (6)$$

- oxygen:

$$\left(\frac{\partial O}{\partial t} \right) = D_o \cdot \left(\frac{\partial^2 O}{\partial z^2} \right) - v \cdot \left(\frac{\partial O}{\partial z} \right) - O \cdot \left(\frac{\partial v}{\partial z} \right) - k_o M O^\delta \quad (7)$$

- solvent:

$$\left(\frac{\partial S}{\partial t} \right) = D_s \cdot \left(\frac{\partial^2 S}{\partial z^2} \right) - v \cdot \left(\frac{\partial S}{\partial z} \right) - S \cdot \left(\frac{\partial v}{\partial z} \right) - k_{trs} S \lambda_{0,0} \quad (8)$$

- initiation radicals:

$$\left(\frac{\partial R_{10}}{\partial t} \right) = D_{R_{10}} \cdot \left(\frac{\partial^2 R_{10}}{\partial z^2} \right) - v \cdot \left(\frac{\partial R_{10}}{\partial z} \right) - R_{10} \cdot \left(\frac{\partial v}{\partial z} \right) + [-k_p M R_{10} - k_{tc} R_{10} \lambda_{0,0} + k_{tdt} (\lambda_{0,0} - R_{10}) - k_{trp} \gamma_{0,0} R_{10} + k_{trs} S (\lambda_{0,0} - R_{10}) - k_{trm} M R_{10}] \quad (9)$$

- moment of order m, n for the free-radicals:

$$\left(\frac{\partial \lambda_{m,n}}{\partial t} \right) = D_{\lambda_{m,n}} \cdot \left(\frac{\partial^2 \lambda_{m,n}}{\partial z^2} \right) - v \cdot \left(\frac{\partial \lambda_{m,n}}{\partial z} \right) - \lambda_{m,n} \cdot \left(\frac{\partial v}{\partial z} \right) + \{ k_o O^\delta M + nk_p M \lambda_{m,n-1} - k_{tc} \lambda_{0,0} \lambda_{m,n} + k_{tdt} (\lambda_{0,0} \delta_{n,0} - \lambda_{m,n}) + k_{trp} \left[\lambda_{0,0} \sum_{j=0}^m \binom{m}{j} \gamma_{j,n+1} - \lambda_{m,n} \gamma_{0,1} \right] + k_{trm} M (\lambda_{0,0} - \lambda_{m,n}) + k_{trs} S (\lambda_{0,0} \delta_{n,0} - \lambda_{m,n}) \} \quad (10)$$

- moment of order m, n for the polymer:

$$\frac{\partial \gamma_{m,n}}{\partial t} = D_{\gamma_{m,n}} \cdot \frac{\partial^2 \gamma_{m,n}}{\partial z^2} - v \cdot \frac{\partial \gamma_{m,n}}{\partial z} - \gamma_{m,n} \cdot \frac{\partial v}{\partial z} + \left[\frac{k_{tc}}{2} \sum_{j=0}^m \sum_{k=0}^j \sum_{i=0}^n \binom{m}{j} \binom{j}{k} \binom{n}{i} (-1)^{j-k} \lambda_{k,i} \lambda_{m-j,n-i} + k_{tdt} \lambda_{m,n} + k_{trm} M \lambda_{m,n} + k_{trs} S \lambda_{m,n} + k_{trp} (\lambda_{m,n} \gamma_{0,1} - \lambda_{0,0} \gamma_{m,n+1}) \right] \quad (11)$$

The high-order moments are obtained by the moment closure technique of Hulburt and Katz (Saidel and Katz, 1968):

$$\mu_{m,3} = \mu_{m,2} \left(2 \frac{\mu_{m,2}}{\mu_{m,1}} - \frac{\mu_{m,1}}{\mu_{m,0}} \right) \quad (12)$$

where $\mu_{m,n}$ represents so much the moments of the free-radicals as the one of the polymer.

The pressure profile was modeled through an uniform pressure drop.

To simplify the analysis of the effect of the axial diffusion, the mixture was treated as a binary system; where the first component was constituted by the smaller molecular weight (monomer, initiator, solvent), while the polymers and the free-radicals constituted the second component.

With the assumption that there are no diffusive effects in the reactor entrance, justified by the high velocities in that reactor zone, the boundary conditions were:

$$\text{At } z = 0: \begin{cases} v = v_0 \\ T = T_0 \\ X = X_0 \end{cases} \quad (13)$$

$$\text{At } z = L: \begin{cases} \left(\frac{\partial T}{\partial z} \right) = 0 \\ \left(\frac{\partial X}{\partial z} \right) = 0 \end{cases} \quad (14)$$

where T represents the temperatures and X the concentrations.

2.3 Model discretization

The nonlinear partial differential equations system, obtained from the dimensionless mass and energy balances, was discretized, along the axial direction, using the spline orthogonal collocation method, where the domain of the axial variable was divided in a series of intervals in the following way:

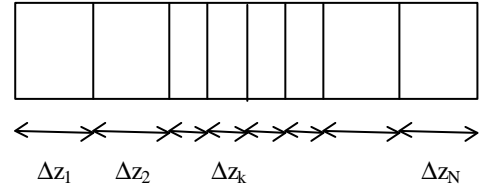


Figure 1. Schematic diagram representing the segmentation of the domain.

It is important to point out that we opted for implementing the spline collocation with variable Δz_k , in order to facilitate the use of smaller intervals in the areas of larger gradient.

Also with the objective to well-describe the behavior of the variables, a variable number of collocation points was adopted in each interval.

Considering that the velocity equation is of first-order and, therefore, it just has one boundary condition, it became necessary to apply a subterfuge so that this variable could be solved with the others: in this particular equation, the orthogonal collocation was used in each one of the intervals in that the reactor was segmented. This is equal to say that, while all the other variables of the system had to submit to the restrictions of equality of the variable and its axial derivative in the border points among intervals (jump points), the velocity just had as restriction the equality of the variable in the jumps.

Applying the polynomial approximation for the i -th collocation point of the k -th spline, results in the following equations:

- velocity:

$$\frac{1}{\Delta z_k} \sum_{j=0}^{P+1} A_{i,j}^k v_j^k + \frac{v_i^k}{\rho_i^k} \left[\frac{T_r}{\Delta z_k} \left(\frac{\partial \rho}{\partial T} \right)_i \sum_{j=0}^{P+1} A_{i,j}^k T_j^k + \left(\frac{\partial \rho}{\partial P} \right)_i \Delta P + \frac{M_r}{\Delta z_k} \left(\frac{\partial \rho}{\partial M} \right)_i \sum_{j=0}^{P+1} A_{i,j}^k M_j^k \right] = 0 \quad (15)$$

- reactor temperature:

$$\frac{dT_i}{dt} = \sum_{j=0}^{P+1} C_{i,j}^k T_j^k + \frac{L}{v_0 \cdot \rho_i^k \cdot c_{p_i}^k} \left[(R_P)_i^k - \frac{4 \cdot U_i^k}{D} (T_i^k - T_{ci}^k) \right] \quad (16)$$

- jacket temperature:

$$\frac{dT_{ci}^k}{dt} = \sum_{j=0}^{P+1} D_{i,j}^k T_j^k - \frac{4 \cdot L \cdot U_i^k}{D_{eq} \cdot v_w \cdot \rho_{wi}^k \cdot c_{pw_i}^k} (T_{ci}^k - T_i^k) \quad (17)$$

- monomer, oxygen, solvent, inert radicals, free-radicals ($\lambda_{0,0}$) and polymer ($\gamma_{0,0}$) concentrations:

$$\frac{dX_i}{dt} = \sum_{j=0}^{P+1} C_{i,j}^k X_j^k - \frac{X_i^k}{\Delta z_k} \sum_{j=0}^{P+1} A_{i,j}^k v_j^k + \frac{L}{v_0} (R_x)_i^k \quad (18)$$

- moments of order m,n for the free-radicals and for the polymer:

$$\frac{d\Lambda_{m,n_i}^k}{dt} = \sum_{j=0}^{P+1} E_{i,j}^k \Lambda_{m,n_j}^k + \frac{(e^{-2n^2 \Lambda_{m,n_i}^k} - 1)}{2n^2 \Delta z_k} \sum_{j=0}^{P+1} A_{i,j}^k v_j^k + \frac{L}{v_0} (R_\Lambda)_i^k \quad (19)$$

$m = 0, 1$ and $n = 1, 2$
where:

$$C_{i,j}^k = \frac{1}{\Delta z_k} \left(\frac{1}{Pe \cdot \Delta z_k} B_{i,j}^k - v_i^k A_{i,j}^k \right)$$

$$D_{i,j}^k = \frac{1}{\Delta z_k} \left(\frac{1}{Pe \cdot \Delta z_k} B_{i,j}^k - A_{i,j}^k \right)$$

$$E_{i,j}^k = \frac{1}{\Delta z_k} \left[\frac{1}{Pe \cdot \Delta z_k} B_{i,j}^k + \left(\frac{2n^2}{Pe} - v_i^k \right) A_{i,j}^k \right]$$

$$A_{i,j}^k = \frac{d\ell_j^k(u)}{du} \Big|_{u=u_i^k}$$

$$B_{i,j}^k = \frac{d^2 \ell_j^k(u)}{du^2} \Big|_{u=u_i^k}$$

$$\ell_j^k(u) = \prod_{\substack{i=0 \\ i \neq j}}^{P+1} \left(\frac{u - u_i^k}{u_j^k - u_i^k} \right), j = 0, 1, 2, \dots, P+1$$

$$k = 1, 2, \dots, N$$

$$i = 0, 1, 2, \dots, P+1$$

where N is the number of intervals (splines) and P the number of collocation points (roots of Jacobi polynomial, $P^{(0,0)}(u)$, of degree P).

The differentiated treatment given to the moments of order $n > 0$ is due to the fact of such variables have suffered a logarithmic change of variable in order to provide a better scaling:

$$\Lambda_{m,n} = \frac{\ln(\mu_{m,n} + 1)}{2n^2} \quad (20)$$

where $\mu_{m,n}$ represents so much the free-radicals moments ($\Lambda_{m,n}$), as the polymer moments ($\gamma_{m,n}$) for $n > 0$.

The boundary conditions were discretized as below:

$$\text{At } z = 0: \begin{cases} v_0^1 = 1 \\ T_0^1 = \frac{T_0}{T_r} \\ X_0^1 = \frac{X_0}{X_r} \end{cases} \quad (21)$$

$$\text{At } z = L: \begin{cases} \sum_{j=0}^{P+1} A_{i,j}^N T_j^N = 0 \\ \sum_{j=0}^{P+1} A_{i,j}^N X_j^N = 0 \end{cases} \quad (22)$$

where T represents the temperatures and X the concentrations.

3. Results and discussion

The resulting algebraic-differential equations system was solved by using the DASSLC code (a C version of DASSL, Secchi and Pereira, 1997). The process parameters and the initial conditions employed in the simulations are listed in Table 1. The physical properties of the reactor mixture and the overall heat transfer coefficient can be found in Chen *et al.* (1976).

Table 1. Operating and initial conditions

Reactor length	1000 m
Internal reactor diameter	5 cm
Equivalent diameter	11 cm
Mixture velocity	400 cm / s
Water velocity	280 cm / s
Reactor pressure	2100 atm
Jacket pressure	30 atm
Pressure drop	150 atm
Initial conditions:	
Reactor temperature	88 °C
Jacket temperature	180 °C
Monomer concentration	2.4×10^{-2} mol / cm ³
Solvent concentration	1.5×10^{-4} mol / cm ³
Oxygen concentration	6.1×10^{-7} mol / cm ³

Figures 2 and 3 illustrate the time evolution of the reactor temperature profile, from an uniform initial profile until to reach the steady-state. In Fig. 2 a fixed Peclet's number of 10 was assumed for all variables, and in Fig. 3 the Peclet was set to 1000 for all of them. These graphs reveals the existence of two expected opposite phenomena. In Fig. 2, the high diffusion of mass and energy, given by low Peclet's numbers, tends to move the profiles to the reactor entrance (as the arrow indicates). This behavior is similar to identified by Agrawal and Han (1975). On the

other side, it can be observed that for high numbers of Peclet (Fig. 3), the convective effects prevails moving the temperature peaks to the end of the reactor. It also can be seen that for short time both number of Peclet have close behavior – although the profile for smaller Peclet exhibits a slowest ascension.

Moreover, Figs. 2 and 3 show that the temperature, in its evolution to steady state, reaches values superior to 350 °C – a safe limit mentioned in the literature (Hollar and Ehrlich, 1983).

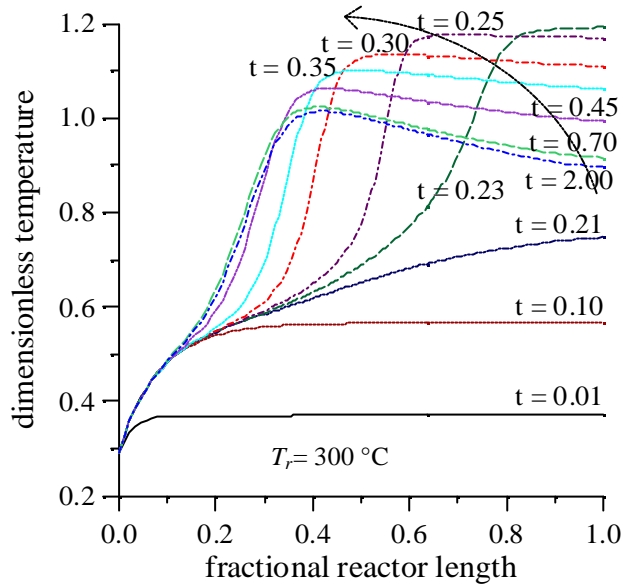


Figure 2. Time evolution of the reactor temperature profile for Pe = 10.

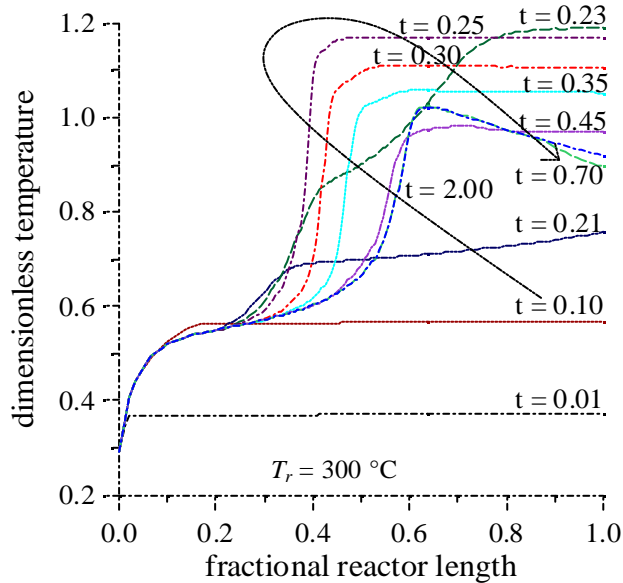


Figure 3. Time evolution of the reactor temperature profile for Pe = 1000.

Figures 4 and 5 show the long time reactor behavior as function of the Peclet's number, assuming all variables having same number of Peclet. These plots show few differences for Peclet greater than 250. In fact, significant variations happen only for Peclet's smaller than 100, confirming the results obtained by Yoon and Rhee (1985).

It also can be seen in Figs. 4 and 5 that the diffusion influence moves the temperature and monomer concentration profiles to the reactor entrance.

In order to verify the individual influence of the heat

and mass Peclet's numbers, the Figs. 6-12 show the long time reactor behavior for Pe ranging from 10 to 1000 for the variable being analyzed, and keeping Pe = 100 for the others. For all situations, when Pe > 100 the diffusion effects are negligible.

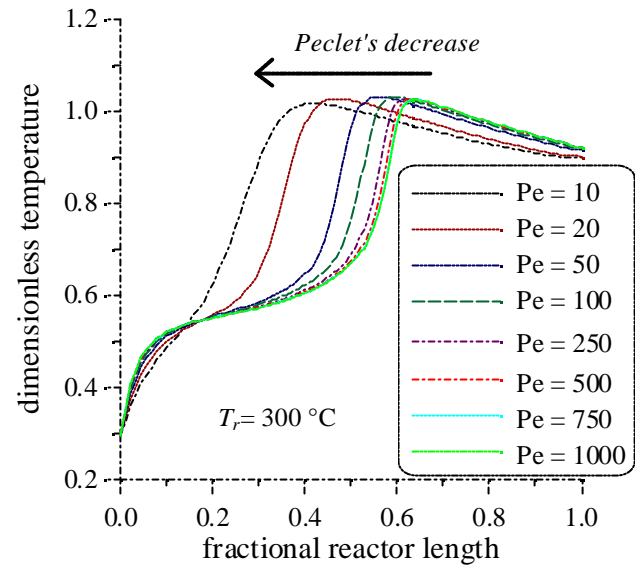


Figure 4. Temperature profile as function of Peclet's number.

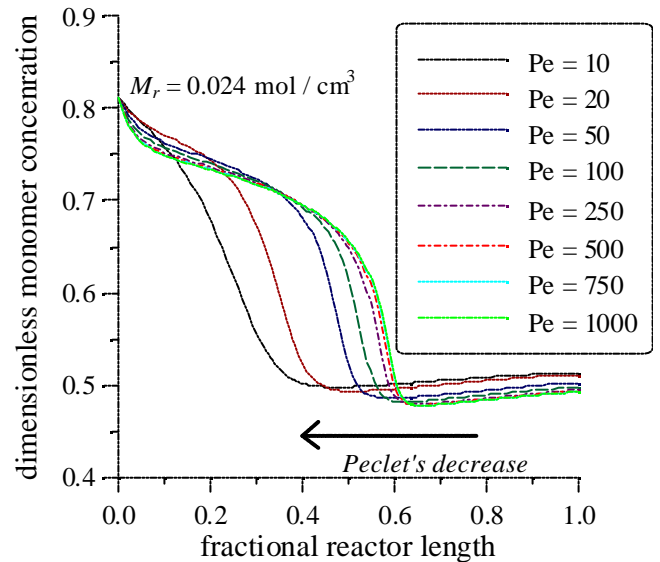


Figure 5. Monomer concentration profile as function of Peclet's number.

Comparing Figs. 6 with Fig. 4, it can be seen that the temperature peak decreases when only the heat Peclet is decreased. This decrease in the temperature peak attests the existence of combined effects of diffusion coefficients. In Fig. 4, that effect is compensated by the increase of monomer conversion, as consequence of the initiator diffusion (effect of the variation of the small-molecules mass Peclet).

Figures 8 and 9 show the reduced influence of the small-molecules mass Peclet in the reactor profiles. This behavior tends to favor the non-diffusion model, because the small molecules are gases, which may have a larger diffusivity, and, consequently, a smaller number of Peclet. Besides, it can be observed that the effects of small-molecules mass Peclet are opposite to the heat Peclet effects. This happens as result of the higher initiator concentrations, provided by diffusion, increasing the temperature peak (Fig. 8) due to higher conversion.

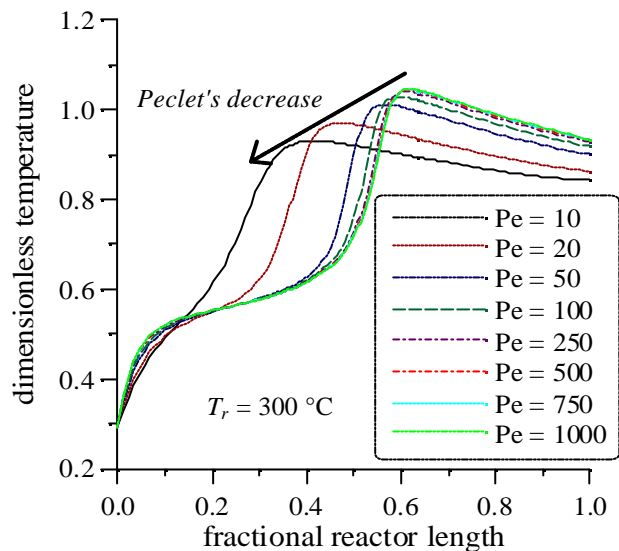


Figure 6. Temperature profile as function of the heat Peclet.

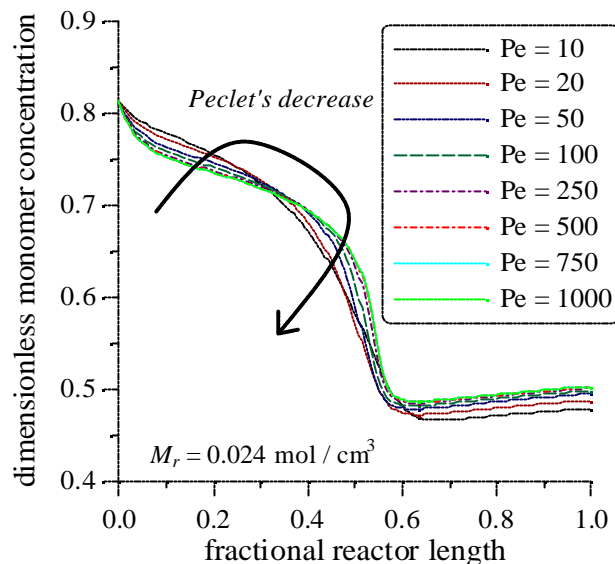


Figure 9. Monomer concentration profile as function of the small-molecules mass Peclet.

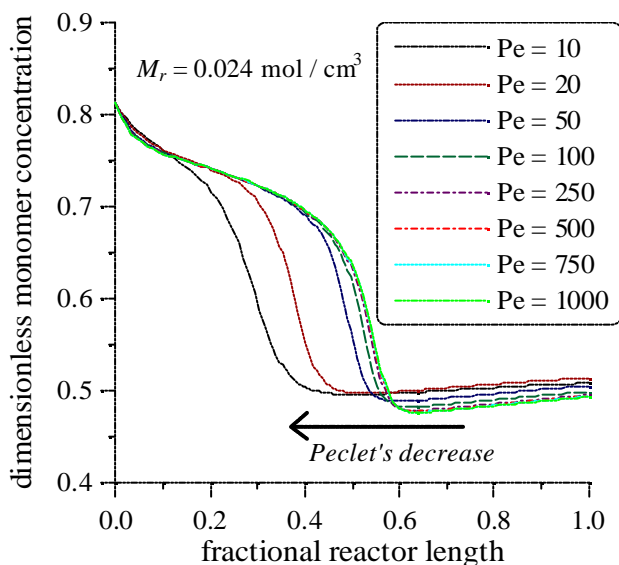


Figure 7. Monomer concentration profile as function of the heat Peclet.

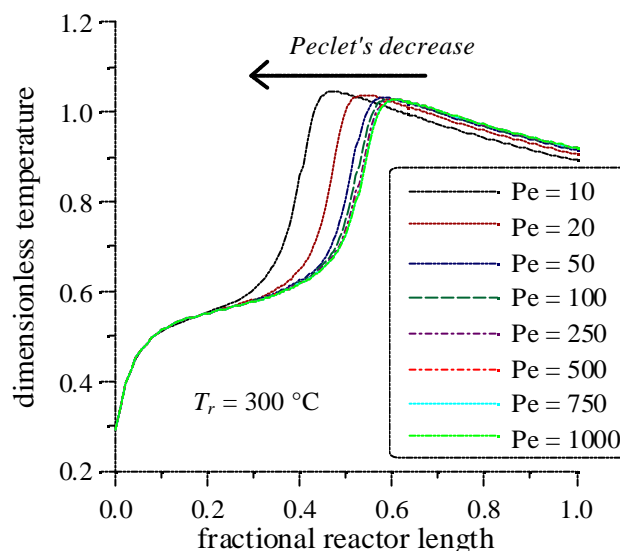


Figure 10. Temperature profile as function of the large-molecules mass Peclet.

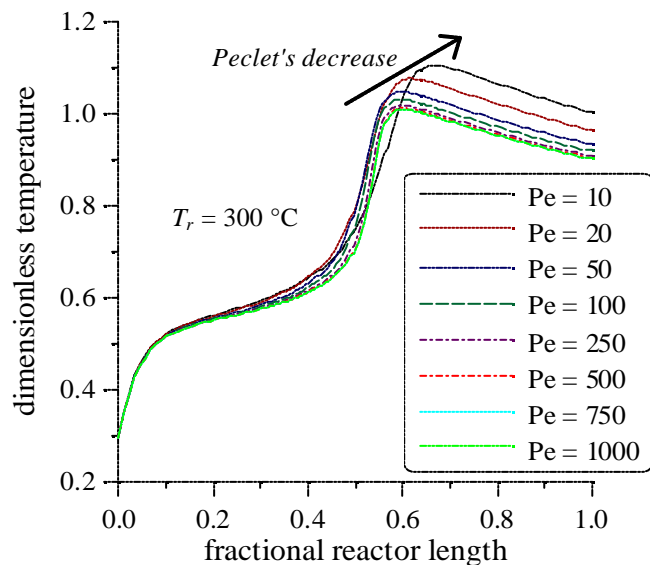


Figure 8. Temperature profile as function of the small-molecules mass Peclet.

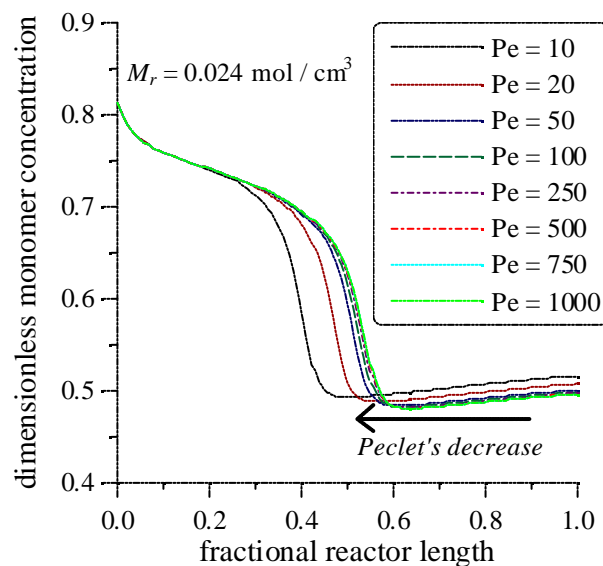


Figure 11. Monomer concentration profile as function of the large-molecules mass Peclet.

The effects of large-molecules mass Peclet (Figs. 10-12) are similar to those of heat Peclet, regarding to the profiles movements to the reactor entrance. This effect may be bigger when the pulse valve effects are taking into account. However, as the polymer has a very small diffusivity, its Peclet's number is very high, which may damp the valve effects.

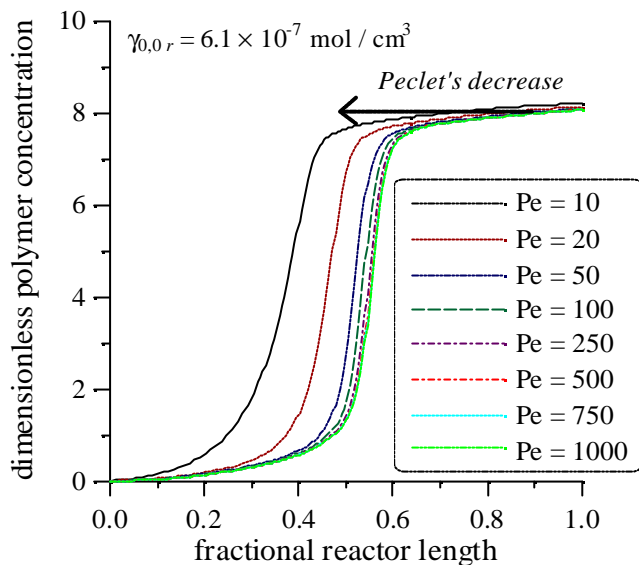


Figure 12. Polymer concentration profile as function of the large-molecules mass Peclet.

4. Conclusions

This work made a more extensive analysis of the influence of the Peclet's number to decide if the axial mixing is important or not. Using a more rigorous model, than the ones presented in the literature to verify that influence, it was proven that number of Peclet larger than 100 can ensure accurate results of models with no axial diffusion.

It was also showed that the components that would have more effects in the axial mixing, due to smaller Peclet's number, have less influence in the reactor profile.

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Notation

c_p, c_{pw}	reactor and jacket specific heat capacities.
D	internal reactor diameter.
D_{eq}	equivalent diameter.
D_X	axial mass diffusivity for component X .
$E, \Delta V^+$	activation energy and volume.
ΔH_r	heat of polymerization reaction.
k_x	Arrhenius' rate constant of reaction x
	$= A \exp\left(\frac{-(E + \Delta V^+ \Delta P_r)}{RT}\right)$
k, k_w	reactor and jacket thermal conductivity.
L	reactor length
M, M_r	monomer concentration and reference monomer concentration.
O	oxygen concentration.

$p_i(x), r_i(x)$	dead polymer and free-radical distribution functions with i long chain branches and x monomer units.
P	reactor pressure.
ΔP	reactor pressure drop.
ΔP_r	pressure difference = $(P - P_{ref})$.
P_{ref}	reference pressure in the rate constants.
Pe_h	Heat Peclet's number = $\rho C_p v_o L / k$.
Pe_m	Mass Peclet's number = $v_o L / D$
R	universal constant of the gases.
R_X	rate of reaction of component X .
S	solvent concentration.
t	time.
T, T_c, T_r	reactor, jacket and reference temperatures.
U	overall heat transfer coefficient.
v, v_w	mixture and water velocities.
x	number of monomer units in the polymer structure.
z	axial distance.
Dz_k	k -th axial element.
δ	oxygen initiation rate order.
$\delta_{m,n}$	Kronecker delta.
$\lambda_{m,n}$	free-radical moment of order m,n .
$\gamma_{m,n}$	dead polymer moment of order m,n .
ρ, ρ_w	reactor and jacket density.

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