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USE OF A TWO-DIMENSIONAL PSEUDO-HOMOGENEOUS MODEL FOR THE STUDY OF TEMPERATURE AND CONVERSION PROFILES DURING A POLYMERIZATION REACTION IN A TUBULAR CHEMICAL REACTOR

UPORABA DVODIMENZIONALNEGA PSEVDOHOMOGENEGA MODELA ZA ŠTUDIJ TEMPERATURE IN PROFILA PRETVORBE MED REAKCIJO POLIMERIZACIJE V CEVASTEM KEMIJSKEM REAKTORJU

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A two-dimensional pseudo-homogeneous model is used to study temperature and conversion profiles during the polymerization reaction of low-density polyethylene (LDPE) in a tubular chemical reactor. This model is integrated with the Runge-Kutta 4th-order semi-implicit method, using orthogonal collocation to transform a system of complex equations into the ordinary differential ones, with respect to the heat and mass transfers involved.

Ethylene polymerization has been simulated over a range of temperatures and pressures and according to the mechanisms of radical polymerization. The results of several tests, carried out under the conditions similar to those of an industrial-scale polymerization, are presented. The influences of the initial temperature T_0, the total pressure P_t and the ratio *L/D* (the main dimensions of the reactor) on the profiles of the temperature and conversion rates are tested and analyzed to predict the behavior and performance of the tubular chemical reactor considered.

The focus was on the effect of an increase in the initial temperature T_0 since such a rise results in a decrease in T_c (hot spot) appearing at the entrance of the reactor on the one hand, and in an improved conversion on the other hand. An opposite effect is observed for P_t since a pressure increase will result in a rapid rise in T_c and a decrease in the conversion. The ranges of pressures and temperatures are thus limited by the system performance: excessive pressures must be avoided and working temperatures must be chosen in the range where the polymerization reaction is very fast; such conditions allow not only a good conversion, but also a resulting polymer with a low crystallinity and, thus, a low density.

In the present work the effect of the *L/D* ratio was also studied in order to find the most suitable ratio that permits the best evacuation of the heat released during the polymerization.

Keywords: modeling, tubular reactor, simulation, low-density polyethylene, pseudo-homogeneous two-dimensional model

Dvodimenzijski psevdohomogeni model je bil uporabljen za študij temperature in profila pretvorbe med reakcijo polimerizacije polietilena z nizko gostoto (LDPE) v cevastem kemijskem reaktorju. V model je bila vključena Runge-Kuttova semiimplicitna metoda 4. reda z uporabo ortogonalne kolokacije za pretvorbo sistema kompleksnih enačb v navadne diferencialne enačbe glede na vključen prenos toplote in mase.

Simulirana je bila polimerizacija etilena v širšem področju temperature in tlaka skladno z mehanizmom radikalne polimerizacije. Predstavljenih je več preizkusov polimerizacije, izvedenih v razmerah, podobnih industrijskim. Preizkušen in analiziran je bil vpliv začetne temperature T_0, celotnega tlaka P_t in razmerja *L/D* (glavne dimenzije reaktorja) na profil temperature in hitrost pretvorbe, da bi bilo mogoče napovedati ponašanje in zmogljivost uporabljenega cevastega reaktorja.

Pozornost je bila usmerjena na učinek povišanja začetne temperature T_0, ker to po eni strani vpliva na znižanje T_c (vroča točka) na vstopu v reaktor, po drugi pa na izboljšanje pretvorbe. Nasproten učinek je bil opažen za P_t, ker se narastek tlaka izraža v hitrem povišanju T_c in zmanjšanju konverzije. Območje tlaka in temperature je torej omejeno z zmogljivostmi sistema: treba se je izogibati prekomernemu tlaku, delovne temperature pa je treba izbrati v območju, kjer je reakcija polimerizacije zelo hitra; take razmere omogočajo dobro konverzijo, in nastali polimer ima majhno kristaliničnost in s tem nizko gostoto.

V tem delu je bilo preučevano tudi razmerje *L/D*, da bi dobili najbolj primerno razmerje, ki omogoča najboljši odvod toplote, ki se sprošča med polimerizacijo.

Ključne besede: modeliranje, cevast reaktor, simulacija, polietilen nizke gostote, psevdohomogen dvodimenzionalni model

1 INTRODUCTION

For many years the production in the chemical industry has been based solely on experience. However, for economic reasons and to avoid extreme conditions of temperature and pressure, the use of simulation methods has become more and more necessary. Indeed, through mathematical models, it is possible to predict relationships between the variations of experimental or production parameters and the practice results.

The polymerization of some unsaturated hydrocarbons, called olefins, is extremely important. The types of polymers obtained consist mainly of low- (LDPE), and high-density polyethylene (HDPE) and polypropylene (PP). LDPE, one of the most frequently produced engineering polymers in the world, is a versatile polymer with a very wide range of applications[1]. Therefore, its polymerization process has been the subject of numerous research works and many studies are still in progress in order to obtain improved LDPE-based materials. In this regard, a better understanding of the polymerization process requires the use of a simulation of the reaction mechanism in order to establish new procedures to reach a better conversion (which is currently 15 % to 35 % in most industrial cases) and to improve the reactor performance based on a model proposed for a tubular chemical reactor. The reactor operating conditions are often difficult to fix. They should ideally be based on the simulation calculations. In other words, an important task is to determine the optimal operating conditions relating to temperature, pressure and conversion for each point of the reactor and this must be done in a rational manner.

Several mathematical models are available for chemical reactors[2–6]. Some researchers and chemists have tried to model and simulate the ethylene polymerization in autoclave reactors[7–9] and in tubular reactors[10,11]. The choice between these models is mostly dictated by the computing resources available and by the knowledge of the values of the parameters required for the simulation.

Tubular chemical reactors have a key role in the chemical industry and they are always part of a larger production system[12]. A tubular reactor for the production of LDPE is usually very long (>1000 m). Despite this reactor length, the conversion is very low (about 15–35 %) and this is due to a high exothermicity of the reaction. Unreacted monomer is separated from the polymer and recycled in the reactor[1,13]. For this reason it is necessary to know the behavior of the reactor, which is contained within the proposal of a set of mathematical models that characterize it[2,5,6,14]. Depending on the precision required, the models can be refined to take into account, in their calculations, the phenomena which are more or less secondary. This will allow presentations that are very close to the real situation.

For this purpose, our present work deals with the use of a two-dimensional pseudo-homogeneous model, based on mass and heat balances[15] in order to study the behavior of a tubular chemical reactor where a polymerization reaction proceeds. The proposed model, together with its resolution method, allows a better understanding of the reaction kinetics, particularly for the LDPE synthesis reaction, and for obtaining the temperature and conversion profiles. All the steps of this process (via the polymer chemistry as well as polymerization engineering) were based on modeling and simulation.

Through the use of a simulation program taking into account all the parameters, several series of calculations are performed over a wide range of temperatures (60–300 °C) and pressures (800–3000 bar). It was found that it is possible to work at the temperatures that allow a moderate conversion (≈35 %), while avoiding an excessive pressure and producing a resulting polymer that has a low degree of crystallinity.

Considering the exothermicity of this reaction, special attention was paid to the operating conditions to ensure the performances, the functioning and the stability control of the reactor. The idea is to have a better control of the heat exchanges by studying the effect of the *L/D* ratio (length or height/diameter of the cylindrical reactor). For such a purpose, it is better to choose a long reactor with a small diameter (i.e., a high *L/D* value).

2 FORMULATION OF THE MATHEMATICAL MODEL

In an elementary volume of the reactor it will be assumed that the system is treated as a homogeneous one and the proposed model is subjected to the following conditions:

1. the system is stationary
   $$\frac{\partial \psi_i}{\partial t} = \frac{\partial \theta}{\partial t} = 0$$
2. the reactor has a cylindrical shape
3. the effect of the volume variation due to the reaction, or the temperature, is negligible
4. the axial, mass and heat dispersions are assumed negligible
   $$\frac{\partial^2 \psi_i}{\partial z^2} = \frac{\partial^2 \theta}{\partial z^2} = 0$$
5. the diffusion and heat-exchange coefficients in the reactor remain constant
6. the pressure is constant along the reactor
7. the temperature of the reactor wall is constant.

The mass and energy balances in the dimensionless form are presented as follows:

$$\frac{\partial \psi_i}{\partial z} = a_{12}\left[\frac{\partial^2 \psi_i}{\partial y^2} + \frac{1}{y}\frac{\partial \psi_i}{\partial y}\right] + b_{12} R(\theta_i, \psi_i) \qquad (1)$$

$$\frac{\partial \theta}{\partial z} = a_{22}\left[\frac{\partial^2 \theta}{\partial y^2} + \frac{1}{y}\frac{\partial \theta}{\partial y}\right] + b_{22} R(\theta_i, \psi_i) \qquad (2)$$

where:

$$a_{12}=\frac{L^2}{Pe_{\mathrm{mr}}\cdot r_0^2} \qquad Pe_{\mathrm{mr}}=\frac{\overline{v}_z\cdot L}{D_{\mathrm{eff,\,r}}}$$

$$a_{22}=\frac{L^2}{Pe_{\mathrm{hr}}\cdot r_0^2} \qquad Pe_{\mathrm{mr}}=\frac{\overline{v}_z\cdot L\cdot \rho_G\cdot C_{P_G}}{D_{\mathrm{eff,\,r}}}$$

$$b_{12}=\frac{L\cdot\rho_{\mathrm{s}}\cdot\nu_i}{C_i^0\cdot\overline{v}_z}\left(\frac{1-\varepsilon}{\varepsilon}\right)$$

$$b_{22}=\frac{L\cdot\rho_{\mathrm{s}}\cdot\nu_i}{T_0\cdot\overline{v}_z\cdot\rho_G\cdot C_{P_G}}(1-\varepsilon)\cdot(-\Delta H_{\mathrm{r}})$$

with the following boundary conditions:

$$\mathrm{z}=0 \quad \Rightarrow \quad \psi=\psi^0, \quad \theta=\theta^0$$

$$\forall(z,y=0) \quad \Rightarrow \quad \frac{\partial\psi_i}{\partial t}=\frac{\partial\theta}{\partial t}=0$$

$$y=\frac{r}{r_0}=1 \quad \Rightarrow \quad \frac{\partial C_i}{\partial r}=\frac{C_i^0}{r_0}\cdot\frac{\partial\psi_i}{\partial y}=0\rightarrow\frac{\partial\psi_i}{\partial y}=0$$

$$-\lambda_{\mathrm{eff,\,r}}\frac{T_0}{r_0}\cdot\frac{\partial\theta}{\partial y}=-h_{\mathrm{w}}\cdot T_0(\theta_{\mathrm{w}}-\theta)$$

$$\Rightarrow-\frac{\partial\theta}{\partial y}=-\frac{h_{\mathrm{w}}T_0r_0}{\lambda_{\mathrm{eff,\,r}}T_0}(\theta_{\mathrm{w}}-\theta)=-B_{i_0}(\theta_{\mathrm{w}}-\theta)$$

with $$\theta_{\mathrm{w}}=\frac{T_{\mathrm{w}}}{T_0}$$

Equations (1) and (2) form a system of parabolic partial derivatives, which are very difficult to resolve. Therefore, the use of the orthogonal collocation method, which assumes a simple form for the radial profiles is advantageous.

For each collocation point y_j we obtain:

$$\frac{\partial\psi_i(z,y_j)}{\partial z}=a_{12}\left[\sum_{k=1}^{N}B_{jk}\cdot\psi_{i,k}+\frac{1}{y_j}\sum_{k=1}^{N}A_{jk}\cdot\psi_{i,k}\right]+b_{12}R(\theta_j,\psi_j) \tag{3}$$

$$\frac{\partial\theta_j}{\partial z}=a_{22}\left[\sum_{k=1}^{N}B_{jk}\cdot\theta_k+\frac{1}{y_j}\sum_{k=1}^{N}A_{jk}\cdot\theta_k\right]+b_{22}R(\theta_j,\psi_j) \tag{4}$$

(j = 2, 3, … n–1)

where $\psi_{i,k}=\psi_i(z,y_k)$

It is clear that equations (3) and (4) are in the form of two first-order differential systems that can be solved by the Runge-Kutta semi-implicit 4th-order method.

By substituting the conversion rate in equations (3) and (4) of the model, we obtain:

$$\begin{aligned}\frac{\partial X_j}{\partial z}&=-a_{12}\left[\sum_{k=1}^{N}B_{jk}\cdot(1-x_k)+\frac{1}{y_j}\sum_{k=1}^{N}A_{jk}\cdot(1-x_k)\right]+b_{12}R(\theta_j,\psi_j)\\ \frac{\partial\theta_j}{\partial z}&=-a_{22}\left[\sum_{k=1}^{N}B_{jk}\cdot\theta_k+\frac{1}{y_j}\sum_{k=1}^{N}A_{jk}\cdot\theta_k\right]+b_{22}R(\theta_j,\psi_j)\end{aligned} \tag{5}$$

(j = 2,3, … N–1)

After the development of these two equations (5) as a form of two systems, we obtain:

$$\begin{aligned}F(j)&=-a_{12}\sum_{k=1}^{N}\overline{A}_{jk}\cdot(1-x_k)+b_{12}R(\theta_j,\psi_j)\\ F(j+Ncol)&=-a_{22}\sum_{k=1}^{N}\overline{A}_{jk}\cdot\theta_k+b_{22}R(\theta_j,\psi_j)\end{aligned} \tag{6}$$

where $$\sum_{k=1}^{N}\overline{A}_{jk}=\sum_{k=1}^{N}\left(B_{jk}+\frac{1}{y_j}A_{jk}\right)$$

The validation of this model, which takes into account differential terms characteristic of the system behavior, has been particularly considered. In this framework a simulation program was developed to predict the behavior of a tubular reactor, where a polymerization reaction takes place under high pressure. The model can be used for a reaction, whose rate is a function of the temperature and concentrations of the reacting chemicals.

3 REACTION KINETICS OF THE ETHYLENE POLYMERIZATION

The reaction system chosen in our work is the radical synthesis of low-density polyethylene (LDPE) in a tubular chemical reactor. LDPE is produced with the radical polymerization of ethylene under high pressure (800–3000 bar) and at the temperatures ranging from 60 °C to 300 °C in the presence of the traces of oxygen and a free radical generator, the azo-bis-isobutyronitrile (AIBN). The reaction is highly exothermic, and one of the first challenges in this process is the removal of the excess heat generated.

The general mechanism of this polymerization involves three main steps, i.e., initiation, propagation, and termination, as shown below:

3.1 Initiation: the step, during which a limited number of active species is created,

$$I\xrightarrow{K_a}2R^*$$

$$R^*+M\xrightarrow{K_a}M_1^*$$

where: I = initiator, R^* = initial free radical, M_1^* = propagating free radical.

3.2 Propagation: successive reactions of monomer molecules to one active or activated end, leading to the growth of the macromolecular chain,

$$M_1^*+M\xrightarrow{K_{p1}}M_2^*$$

$$M_2^*+M\xrightarrow{K_{p2}}M_3^*$$

Or in general: $M_n^*+M\xrightarrow{K_{pn}}M_{n+1}^*$

where: K_{p1}, K_{p2}, …, K_{pn} are propagation constants.

3.3 Termination: deactivation of the species or the active end, and the cessation of the chain growth.

$M_n^*+M_m^*\xrightarrow{K_{tc}}P_{n+m}$ (by combination or coupling)

$$M_n^* + M_m^* \xrightarrow{K_{td}} P_n + P_m \quad \text{(by disproportionation)}$$

The main step of the polymerization is the chain propagation (including several elementary reactions), when the macromolecule is built.

The successive addition of monomer M during the propagation can be generally described as follows:

$$M_n^* + M \xrightarrow{K_p} M_{n+1}^*$$

The expression of the propagation speed is then:

$$V_p = K_p \cdot (M)\sqrt{f \cdot K_d / K_t} \cdot \sqrt{(I)}$$

V_p can also be expressed generally as follows:

$$V_p = K_p \cdot (M)\sqrt{V_i / 2K_t}$$

It is to be noted that the values of various parameters (technology, kinetics, thermodynamics, etc.) are taken from the literature[16–20]. Thus, we have all the data required to calculate the theoretical profiles of the temperature and the conversion in the reactor (**Tables 1** and **2**).

Table 1: Operating conditions used for simulation
Tabela 1: Delovni pogoji, uporabljeni za simulacijo

L = 1390 m	R = 8.3 J mol^{-1} K^{-1}
D = 0.05 m	T_w = 400 K
V_{ms} = 0.20 m s^{-1}	P_t = 2250 bar
ρ_c = 1900 kg m^{-3}	D_{eff} = 6 · 10^{-5} cm^2 s^{-1}
ρ_g = 530 kg m^{-3}	H_w = 81.677 · 10^{-3} J cm^{-2} °C^{-1} s^{-1}
C_p = 3.135 J g^{-1} °C^{-1}	λ_{eff} = 0.02 W m^{-1} K^{-1}
C_{A0} = 2.47 · 10^{-4} mol L^{-1}	ΔH_r = –89.87 kJ mol^{-1}
C_{M0} = 16.75 mol L^{-1}	ε = 0.5

Table 2: Kinetic parameters of the radical polymerization of ethylene (AIBN at 60 °C)[20]
Tabela 2: Kinetični parametri radikalne polimerizacije etilena (AIBN pri 60 °C)[20]

K_d = 0.845 · 10^{-5} s^{-1}	E_d = 123 kJ mol^{-1}
K_p = 0.243 · 10^3 L mol^{-1} s^{-1}	E_p = 18.4 kJ mol^{-1}
K_t = 54 · 10^7 L mol^{-1} s^{-1}	E_t = 1.3 kJ mol^{-1}

4 RESULTS AND DISCUSSION

Knowing the great importance of some techno-economic parameters in the industry using chemical reactors, we propose to study the influence of three parameters – the initial temperature T_0, the total pressure P_t and the ratio of the reactor's main dimensions (L/D) – on the profiles of the temperature and conversion rates, to establish the optimal working conditions. It is often difficult to control, at the same time, these three parameters and to obtain reproducible results. Therefore, it is necessary to vary one parameter only while maintaining the other two constant.

Some chemical reactors can certainly work at a high temperature or a high pressure, but because of their technology implementation and geometry, it is more difficult to have, simultaneously, a high operating pressure and an elevated reaction temperature. For this reason, we are mainly interested in obtaining information about the physical state of the reaction mixture.

The purpose is to clarify the influence of physical conditions – mainly temperature T_0 and pressure P_t as well as the L/D ratio – on the reactor functioning in order to know its behavior and also to avoid the phenomenon of thermal runaway due to excessive temperature resulting from a bad heat exchange that leads to a thermal instability.

After the simulation treatments of our models, the following results are obtained:

4.1 Influence of the initial temperature (T_0)

In all industrial installations, the temperature measurement is particularly important to ensure the performance and to monitor the smooth running of the operations. The T_0 factor is a basic parameter, from which we deduce most of the other reaction parameters such as pressure, mixture composition and geometry of the reactor (the optimal ratio L/D)[21].

Changing the initial temperature T_0, while maintaining the other two parameters, P_t and L/D, constant, affects the dimensionless temperature profiles θ and the rate of conversion x.

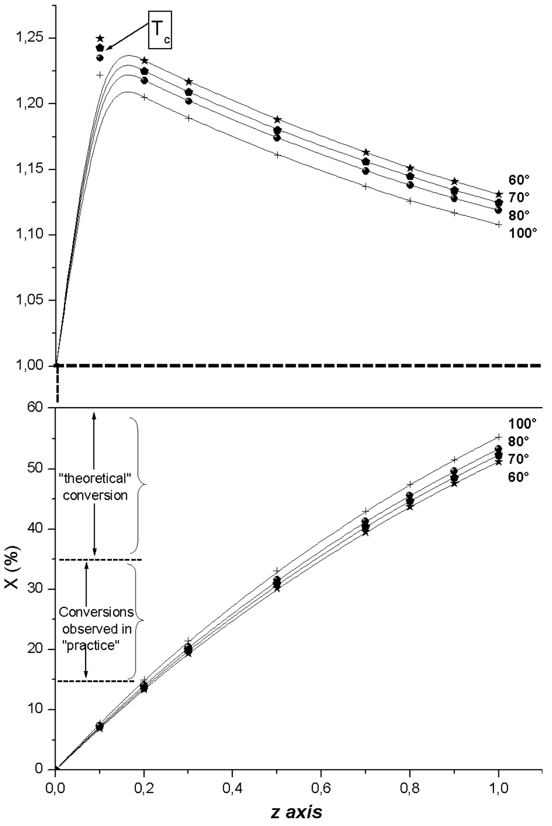

Figure 1: Variations of dimensionless temperature θ and conversion x along the z-axis of the reactor for various values of T_0
Slika 1: Spreminjanje brezdimenzijske temperature θ in konverzije x vzdolž z-osi reaktorja za različne vrednosti T_0

Figure 1 shows a clear hotspot T_c, right at the entrance of the reactor (z = 0.10), for each value of T_0 considered, where we may have to cope with the problems of thermal instability that most often occur after a failure of the cooling system (placed against the outer wall of the reactor). The value of T_C decreases with an increase in T_0, which means that the dimensionless temperature θ decreases with an increase in the initial temperature T_0 at any position along the reactor z-axis. This increase of T_0 has the advantage of increasing the conversion, that is to say, the polymer molecular weight and viscosity. In general, the conversion increases slightly with increasing T_0 for any value of z. The range of temperature T_0 was limited with the performance of the system that allows both relatively fast reaction rates and relatively good conversions, leading to a polymer having a low crystalline content and a low density.

It is noticeable that the temperature, after reaching the maximum value of T_C for each T_0, decreases along the z-axis, which allows us to conclude that:

- The reaction is greatly accelerated by a rise in the temperature at the entrance of the reactor, where the polymerization rate is maximum. The heat generated is removed through a cooling liquid (usually water) to reduce the occurrence of hot spots, T_C, and to obtain a uniform distribution of the temperature inside the reactor.
- The initiation reaction has a strong thermal energy resulting in the "hot spot" observed during this step. We can say that it is likely that the activation energy of the initiation (E_d) is much superior to the other activation energies (propagation (E_p) and termination (E_t)); in our case, the initiation is the result of a thermal decomposition (**Table 2**).

Because the velocity profiles are considered flat, i.e., the flow in our reactor is assumed to be a plug flow, the transit time is the same for each species. For this reason, the radial temperature θ and the conversion (**Figure 2**) remain constant.

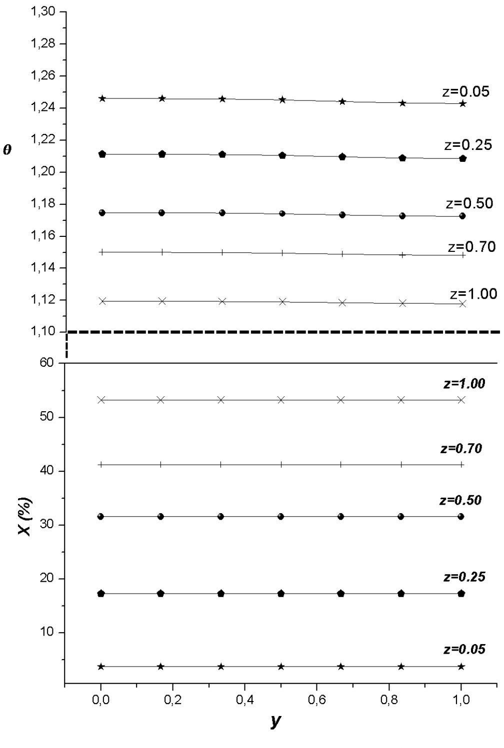

Figure 2: Variations of dimensionless temperature θ and conversion x as a function of radial direction y of the reactor for various positions along the z-axis

Slika 2: Spreminjanje brezdimenzijske temperature θ in konverzije x kot funkcije radialne smeri y v reaktorju za različne položaje vzdolž z-osi

4.2 Influence of the total pressure (P_t)

High-pressure polymerization of ethylene in tubular reactors is an important commercial process[22]. The pressure is a factor involved directly in the reaction kinetics through the reaction enthalpy as given by the following expression[19]:

$$\Delta H = 115.3 \cdot [718.6 + (0.05 \cdot T_0) + (0.025 \cdot P_t)] \ /(\mathrm{J \cdot g^{-1} \cdot mol^{-1}})$$

To better highlight the effect of the total pressure on the temperature and conversion profiles, the simulations are made assuming that this pressure remains constant along the reactor (an assumption of no charges losses).

The results shown in **Figure 3** (the profiles of dimensionless temperature θ and the rate of conversion x as a

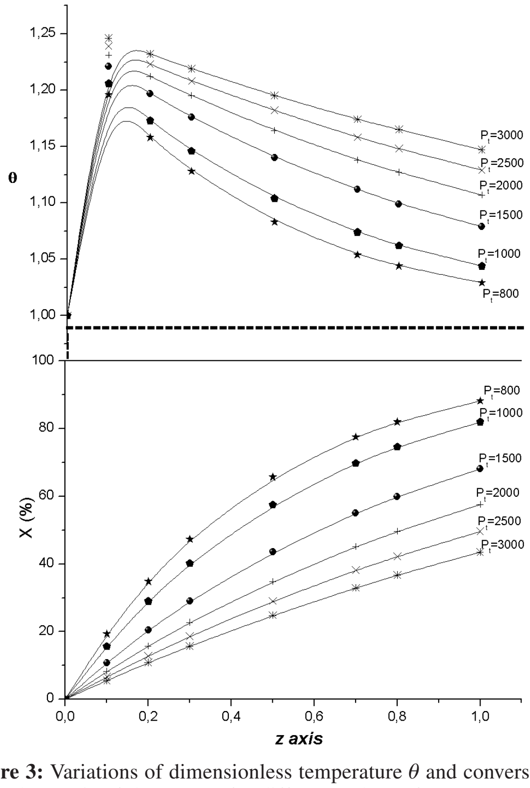

Figure 3: Variations of dimensionless temperature θ and conversion x along the z-axis of the reactor for different values of P_t

Slika 3: Spreminjanje brezdimenzijske temperature θ in konverzije x vzdolž z-osi reaktorja za različne vrednosti P_t

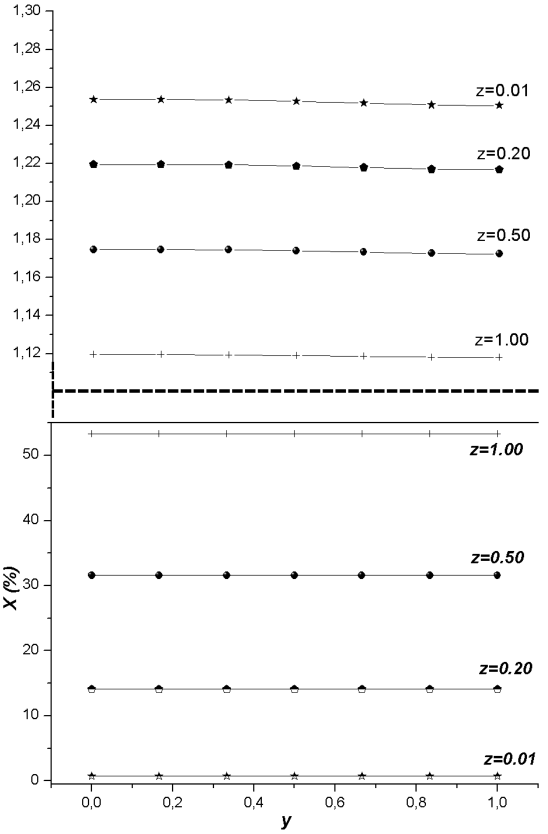

Figure 4: Variations of dimensionless temperature θ and conversion x as a function of radial direction y of the reactor for various positions along the z-axis

Slika 4: Spreminjanje brezdimenzijske temperature θ in konverzije x kot funkcije radialne smeri y reaktorja za različne pozicije vzdolž z-osi

function of the pressure along the z-axis of the reactor) confirm the influence of the pressure on these two parameters. Such results are in agreement with the expectations: when pressure P_t increases the conveying speeds are highly accelerated and the temperatures are higher, while the conversion rate decreases regardless of the position along the z-axis of the reactor. This conversion decrease can be explained as follows: a pressure rise increases the conveying speed that, in turn, limits the cross-linking reactions and deposit formation (crust) on the wall (these reactions cause the formation of deposits that prevent adequate heat transfer).

The range of the total pressure P_t has been limited by the performance of the system in order to avoid excessive pressure (≤3000 bar) and prevent an overheating of the system. It may be noticed that, when working at high pressures, hot spots become more consistent, thus potentially leading to a runaway of the reactor. For this reason, the heat must be controlled precisely to prevent such a runaway and to better control the molecular weight distribution of the polymer.

Here we also notice that the radial temperature θ and the rate of conversion x (**Figure 4**) remain practically constant along the radial direction y. This uniformity of the temperature and the conversion rate is due to the fact that the velocity profiles are considered flat, i.e., the flow in our reactor is assumed to be a plug flow, therefore, the transit time is the same for each species.

4.3 Influence of the ratio (L/D)

Equipment geometry and dimensions are very important because, in the industrial production, all the operations are performed in a reactor having certain geometric dimensions. In practice these parameters (characteristics) are designated as "the main dimensions", and can be represented by the length (or height) L and the diameter D of the reactor. It is common to use a dimensionless number, characteristic of the device, designated by the ratio (L/D). Knowing the value of the L/D ratio is very important, because, from its value, one can deduce, for example, the type of a flow (i.e., the Reynolds Number) and also the reactor similarity that should then be considered.

If the ratio (L/D) increases, the particle motion becomes increasingly ordered, i.e., the axial diffusion is less important. The transition (similarity) between a tubular reactor and a plug-flow reactor can then be characterized with the axial diffusion, i.e., with an increase in the ratio (L/D). Indeed, the tubular reactor is used only if the residual heat is moderate. In the opposite case, significant radial temperature differences will appear. These would cause radial gradients of the polymerization rate and the viscosity that would impair the quality of the polymer.

Figures 5 and **6** show that an increase in the ratio (L/D) leads to the reduction of the temperature, which, in turn, causes an increase in the conversion rate, and this can be observed for each z position along the reactor axis. This allows us to say that a large value of the ratio (L/D) greatly influences the homogenization of the reaction medium with molecular diffusion, and that this

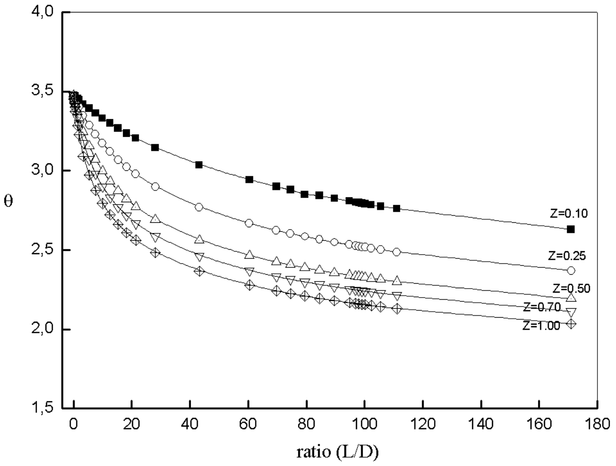

Figure 5: Variations of dimensionless temperature versus ratio (L/D) for different positions along the z-axis

Slika 5: Spreminjanje brezdimenzijske temperature z razmerjem L/D za različne pozicije vzdolž z-osi

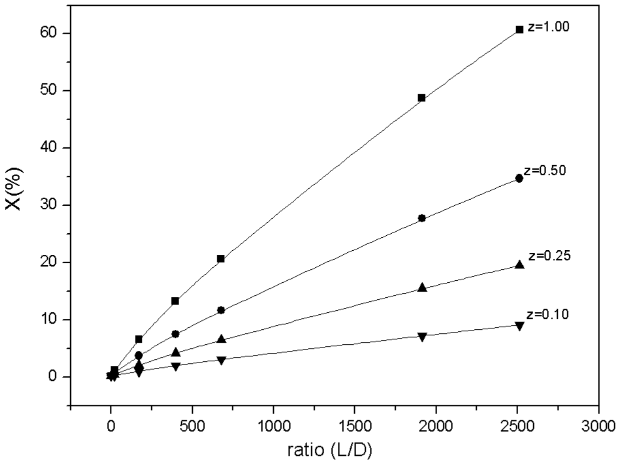

Figure 6: Variations of conversion rate x versus ratio (*L/D*) for different positions along the *z*-axis

Slika 6: Spreminjanje hitrosti konverzije *x* z razmerjem *L/D* za različne pozicije vzdolž *z*-osi

property makes the tubular reactors more adapted to the study and implementation of highly exothermic reactions.

5 CONCLUSION

Taking into account all the results obtained, we observe that:

- Measurements of temperatures, pressures and main dimensions of the reactor are particularly important to ensure the performance and monitoring of the functioning of the ongoing operations.
- The two-dimensional model formulation and the development of the appropriate calculation programs led us to a better understanding of the evolution of the temperature and conversion rate during the synthesis reaction of low-density polyethylene in a tubular chemical reactor.
- The proposed model (two dimensional) and the resolution method (Runge-Kutta semi-implicit 4th-order method), applied to the process of polymerization of LDPE, allow the obtention and the prediction of the influence of the initial temperature T_0, the total pressure P_t and the reactor dimensions (ratio *L/D*) on the temperature and conversion-rate profiles in a tubular chemical reactor in a steady state.

The proposed model as well as the solving method are general enough to be applied to many industrial chemical reactions, with respect to the materials (production of polymers, for instance) and the materials engineering (reactor dimensions and operating conditions). They allow a study and a comparison of the profiles (temperature and conversion) for different operating conditions of the reactor. Thus, they appear to be able to predict, with a reasonable accuracy, the behavior of the reactor in question.

Nomenclature

Bi_θ	Biot number at the reactor wall
C_i^0	initial concentration of the i component [mol L^{-1}]
$C_{P\,G}$, $C_{P\,S}$	specific heat at a constant pressure of gas, solid [J kg^{-1} K^{-1}]
D_{eff}	effective diffusivity [m^2 s^{-1}]
D_A	diffusion coefficient of the component A [m^2 s^{-1}]
E	activation energy [J mol^{-1}]
F	efficiency factor of the initiator
h_W	coefficient of the overall heat transfer to the wall [W m^{-2} K^{-1}]
(I)	initiator concentration [mol L^{-1}]
K_p	propagation rate constant [L mol^1 s^{-1}]
K_d	rate constant for the initiator dissociation [s^{-1}]
K_a	rate constant for the monomer addition [s^{-1}]
K_t	termination rate constant [L mol^1 s^{-1}]
K_{tc}	termination rate constant by combination [L mol^1 s^{-1}]
K_{td}	termination rate constant by disproportionation [L mol^1 s^{-1}]
L	reactor length [m]
M	monomer
(M)	monomer concentration M [mol L^{-1}]
M^*	monomer radical
P_t	total pressure [bar]
Pe	Peclet number
Pe_{mr}	Peclet number on the radial matter
Pe_{hr}	Peclet number of the radial heat
r	radial distance [m]
R_i	reaction rate [mol kg^{-1} s^{-1}]
t	time [s]
T	temperature [K]
T_0	initial temperature [K]
T_W	temperature of the wall [K]
V_p	speed of the propagation (polymerization) [mol L^{-1} s^{-1}]
V_i	initiation rate
$\overline{v}_z$	average axial velocity
z	dimensionless axial distance
Y	dimensionless radial distance
Z	axial distance [m]
λeff	effective thermal conductivity [W m^{-1} K^{-1}]
ρ	density [kg m^{-3}]
ρ_s	volume density of the catalyst ($\rho_s = m/V_s$) [kg m^{-3}]
ρ_G	volume density of gas
ρ_a	bulk density ($\rho_a = m/V$) [kg m^{-3}]
ε	porosity
ψ_i	dimensionless concentration ($\psi_i = C_i/C_{i0}$)
θ	dimensionless temperature ($\theta = T/T_0$)
θ_W	dimensionless temperature of the wall ($\theta_W = T_W/T_0$)
ν_i	stoichiometric coefficient
x	conversion rate [%]
ΔH_r^0	heat released during the reaction [J mol^{-1}]

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