



4th International Conference on Process Engineering and Advanced Materials

Simulation Studies of Low-Density Polyethylene Production in a Tubular Reactor

Ashraf Azmi and Norashid Aziz^{a,*}

^a*School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, MALAYSIA.*

Abstract

This paper deals with the model based of an industrial low-density polyethylene (LDPE) tubular reactor. As the LDPE industry becomes more competitive, manufacturers have to come out with solutions to debottleneck the reactor output while abiding to the stringent product specification. In other words, they have to deal with maximization of the production (maximization of the monomer conversion for a given feed flow rate) and minimization of unwanted product (ethyl, butyl, vinyl and vinylidene groups), while maintaining the polymer product quality with regards to its molecular weight distribution (MWD). To achieve these goals, understanding the effects of operating variables manipulation as well as the dynamic behavior of tubular reactor is essential to develop high performance tubular reactor. In this study, the dynamic model of a tubular reactor for the production of low-density polyethylene (LDPE) is simulated using MATLAB R2015a® in order to predict the temperature profile and monomer conversion percentage along the tubular reactor. The model consists of feed stream, reactor jacket, initiator injector and outlet stream. Several operating variables are involved, notably the feed flow rates, the inlet pressure and temperature with varying parameters to analyze the effect on the reactor productivity. Plots of reactor temperature profile and monomer conversion percentage are presented and from the result, it can be concluded that feed temperature gives significant impact as it effects monomer conversion rate.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: LDPE; polymerization; tubular reactor; ethylene

1. Introduction

Low-density polyethylene (LDPE) is an important commodity polymer and is widely used for a large number of applications including packaging, adhesives, coatings and films. Extraordinary electrical and impact properties, chemical inertness and moisture resistance (defiance) have made LDPE become exclusive and the demand has been reported to increase globally [1,2]. In general, LDPE is commonly produced in either tubular reactors or stirred autoclave vessels, however; this work concentrates on the production of LDPE in tubular reactor only.

LDPE, in the density range of 915 – 925 kg/m³, is manufactured commercially in high-pressure free radical polymerization reactors in the presence of mixture of initiators (i.e., peroxides), typically at pressures of 101325 – 303975 kPa and temperatures

* Corresponding author. Tel.: +604-5996457.
E-mail address: chnaziz@usm.my

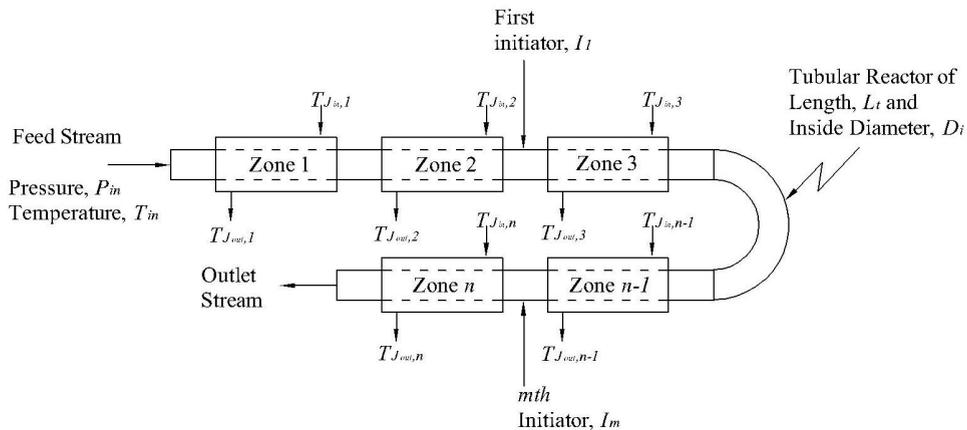


Fig. 1. Schematic diagram of an industrial LDPE tubular reactor [3]

of 373.15 – 598.15 K. A typical high-pressure LDPE tubular reactor's length ranging from 500 to 1500 m is characterized by very large ratios of length to diameter (L/D) from 1 – 6×10^4 . Schematic diagram of a typical industrial LDPE tubular reactor is shown in Figure 1.

Heat prerequisite (balance) of LDPE tubular reactor is a key factor in a commercial polymerization process. The initial section of the tubular reactor behaves as a preheater, where ethylene with another feed stream is heated by steam or water up to the optimal temperature for thermal decomposition of initiators. According to Agrawal et al. [3], this temperature relies on initiator used, ranging from 190°C for oxygen to 140°C for a peroxydicarbonate (peroxides).

The subsequent sections of the tubular reactor act as a product cooler. Ethylene polymerization is a highly exothermic reaction. The heat of reaction during polymerization reaction is partially transferred through the reactor wall by the heat-transfer fluid, which flows inside a reactor jacket. Nearly half of the heat generated via the reaction is eliminated by the cooling fluid flowing in the reactor jacket co- or counter currently to the reaction fluid [4]. The heat of reaction, if not removed or transferred, can lead to runaway condition inside the tubular reactor. Monitoring the pressure alongside the tubular reactor is crucial in order to identify the occurrence of fouling caused by precipitated polyethylene.

Numerous studies have been conducted to model and simulate LDPE tubular reactors with the aim of maximizing the monomer conversion, minimizing the unwanted product (ethyl, butyl, vinyl and vinylidene groups); while maintaining the polymer product quality with regards to its molecular weight distribution (MWD). Driven by this aims and the facts that heat and pressure play a key role in ethylene polymerization, in substantial studies, dynamic models were developed for LDPE polymerization in tubular reactor.

Chen et al. [5] have investigated the correlation between reactor temperature profiles with regards to the jacket temperature variations where the feed temperature was kept constant. However, for simplification purpose, only five reaction mechanisms were included in their model, namely initiation, propagation, termination by combination, termination by thermal degradation, and chain transfer to polymer.

Later study by Gupta et al. [6] highlighted the effect of feed and jacket temperatures variation along the tubular reactor. In their study, eight kinetic mechanisms were applied and it was observed that monomer thermal initiation mechanism was ignored. Asteasuain et al. [7] stressed that monomer thermal initiation must necessarily be kept in kinetic mechanism due to its importance at runaway condition. Motivated by this, in this present study, the effect of feed temperature variations on reactor temperature profile alongside the tubular reactor is studied quantitatively with the improvement in kinetic scheme as a new contribution.

2. Model Formulation

The tubular reactor is modeled based on ideal plug flow assumption with no axial mixing [5,6,8]. For simplification and to avoid any complications, the model is utilized on single feed and initiator injection point. The pressure inside reactor is kept constant throughout the reactor since the pressure drops less than about 10 percent of the mean value are not significant [6]. Pulse valve effect is not included in the model as inferred from pilot plant studies by Donati et al. [9].

Homogenous phase (single phase) of ethylene and polyethylene is assumed as suggested by Ehrlich and Mortimer [10] that, at typical industrial temperatures and pressures encountered in polymerization processes, the monomer and polymer, form and exists as a single fluid phase. The heat capacity of reaction mixture is represented as total heat capacities of pure components [8]. For simplification purpose, the tubular reactor is modeled as single monomer gas feed with single injections of initiator. The model utilized the axial length (z) of tubular reactor as the independent variable, and the ordinary differential equations (ODE) are integrated along the reactor length.

Table 1. The kinetic mechanism used in this study

Reaction	Kinetic Mechanism	Equation
Peroxide initiation	$I \xrightarrow{K_d} 2R_{in}$	(1)
Monomer thermal initiation	$3M \xrightarrow{K_{th}} 2R_1$	(2)
Propagation	$R_1 + M \xrightarrow{K_p} R_{l+1}$	(3)
Termination by combination	$R_l + R_k \xrightarrow{K_{tc}} P_{l+k}$	(4)
Thermal degradation	$R_{l+1} \xrightarrow{K_{thd}} P_l + R_1$	(5)
Chain transfer to monomer	$R_l + M \xrightarrow{K_{trm}} P_l + R_1$	(6)
Chain transfer to polymer	$R_l + P_k \xrightarrow{kK_{trp}} P_l + R_k$	(7)
Chain transfer to transfer agent	$R_l + S \xrightarrow{K_{trs}} P_l + R_1$	(8)
β -Scission of secondary radical	$R_{l+1} \xrightarrow{K_{\beta}} P_l + R_1$	(9)
β -Scission of tertiary radical	$R_{l+1} \xrightarrow{K_{\beta 1}} P_l + R_1$	(10)

Volumetric flow rate of jacket fluid was kept constant [6,8]. Initiator used in small concentration amounts, is assumed to give negligible effect on the flow dynamics and heat transfer of reaction mixture. Initiators efficiency value is assumed to be unity. Overall heat transfer coefficient, U conform to the approach of Chen et al. [5] and Gupta et al. [6]. The reaction mechanism which is fundamental to one model, gives significant effect to the reaction temperature profiles and molecular properties of polymer. The reaction mechanism applied in this study is given in Table 1. It largely incorporates most of the reactions where the rate constants are obtainable in the Yao et al. [8].

To date, there are no mutual agreements among researchers on the fixation of reaction mechanism in one model. It is largely dependent on the reactor temperature profiles and molecular properties of polymer. Azmi and Aziz [1] summed up the justification of inclusion or exclusion of reaction mechanism given by numerous researchers in their paper. The mass and energy balances of various species in a tubular reactor model with the physical properties varying with z are given in Table 2. The rate constants are listed in Table 3. Most of the equations have been taken from Chen et al. [5] and Gupta et al. [6]. An overview of modeling studies on LDPE reactors available in the open literature indicates significant inconsistencies among researchers for kinetic constants.

2.1. Simulation

MATLAB R2015a® is used to solve the ODEs listed in Table 2. With regards to computational aspects, the axial length (z) of plug flow reactor (PFR) model is divided into 2 intervals to provide stability, thus allowing an effective computational execution. The differential equations are solved using ode15s solver. This solver is chosen due to its suitability for stiff differential equations. Furthermore ode15s is a variable order solver based on the numerical differentiation formulas (NDFs). The value of the parameters used in this simulation which is typically identical to the industrial reactors, are listed in Table 3.

3. Results and Discussion

The simulation results of the developed model for the high pressure tubular reactor are presented in Figures 2 (a) and (b). Figure 2 (a) show the temperature profiles of tubular reactor along the axial distance of reactor. The equations given in Table 2 constituting a set of ordinary differential equation is applied along with other relevant equations to obtain the temperature profile. Results obtained from this simulation are found to be close to those reported by Gupta et al. [6] and Yao et al. [8] who used slightly different set of equations and operating conditions.

As soon as monomer is introduced in the tubular reactor inlet, reaction mixture is heat up to the optimal temperature for initiator injection. Initiator decomposition is temperature dependent and could be spoiled if the reaction temperature exceeds the half-life of the applied initiator [3]. From Figure 2 (a), it is obviously seen that the reaction occur as soon as the reaction mixture reach the optimum temperature for the initiator decomposition process. Curve number 3 reacted earlier compared to the other curves, due to its high feed temperature which is 160°C. This is true since radical formation via initiator decomposition process is largely dependent on the half-life temperature ranges; it is believed that as soon as the reacting mixture in curve number 3 elapse the half-life temperature of initiator, propagation reaction immediately occurred. As a proof, a rapid increase in the reaction temperature profile is observed in this zone. This is due to the exothermic nature of the polymerization reaction.

Table 2. Model Equations for the LDPE Tubular Reactor

Descriptions	Equation	Equation
Overall mass balance	$\frac{dv}{dz} = -\frac{v}{\rho} \left(\frac{d\rho}{dz} \right)$	(11)
Initiator balance	$v \frac{dC_{i_m}}{dz} = (-2fK_{d_m}C_{i_m} - C_{i_m} \frac{dv}{dz}) \quad \therefore \text{for } m = 1, 2$	(12)
Monomer balance	$v \frac{dC_M}{dz} = (2K_{th}C_M^3 - K_{trm}C_M\lambda_0 - C_M \frac{dv}{dz})$	(13)
Solvent balance	$v \frac{dC_S}{dz} = (-K_{trs}C_S\lambda_0 - C_S \frac{dv}{dz})$	(14)
Reactor temperature	$\frac{dT}{dz} = \frac{1}{\rho C_p v} \left[-\Delta H K_p C_M \lambda_{00} - \frac{4U(T - T_j)}{D} \right]$	(15)
Reaction mixture density variation	$\frac{d\rho}{dz} = \frac{\partial \rho}{\partial T} \frac{dT}{dz} + \frac{\partial \rho}{\partial C_M} \frac{dC_M}{dz}$	(16)
where		(17)
	$\frac{\partial \rho}{\partial T} = \frac{1.436 \times 10^{-6} C_M - 2.5245 \times 10^{-4} + (31.6967 - 1.25 C_M) \times 10^{-9} T - 9.98877 \times 10^{-11} T^2}{(0.71 - 4.475 \times 10^{-4} T)^2 (0.949 + 4.988 \times 10^{-4} T)^2}$	(18)
and		(19)
	$\frac{\partial \rho}{\partial C_M} = 0.028 \left(\frac{1 - 0.71 - 4.475 \times 10^{-4} T}{0.949 + 4.988 \times 10^{-4} T} \right)$	(19)
Overall heat transfer coefficient	$U^{-1} = h_i^{-1} + h_w^{-1}$	(19)
Reaction mixture density (g/cm ³)	$\rho = \frac{1 + 0.028 C_M (V_p - V_M)}{V_p}$	(20)
Specific heat of reactant mixture (cal/g.K)	$C_p = 0.518 w_m + (1.041 + 8.3 \times 10^{-4}) w_p$	(21)
Heat of reaction (cal/mol)	$-\Delta H = 23000$	(22)
Moment of live polymer radical	$\lambda_0 = \sqrt{\frac{2fK_{d_m}C_{i_m} + 2K_{th}C_M^3}{K_{tc}}}$	(23)
Reactor side heat transfer coefficient (cal/cm ² .s.K)	$h_i = \frac{K(Nu)}{D_i}$	(24)
Thermal conductivity (cal/cm.s.K)	$K = (5w_m + 3.5w_p) \times 10^{-4}$	(25)
Nusselt Number	$Nu = 0.026 Re^{0.8} Pr^{0.33}$	(26)
Reynolds Number	$Re = \frac{\rho D_i v}{A_s \eta_s}$	(27)
Viscosity of reactant mixture, Poise	$\eta_s = \eta_r \eta_o$	(28)
Relative viscosity of monomer	$\eta_r = 10^{0.0313 \sqrt{\mu_{00}^{-1} \mu_{00}^3}}$	(29)
Viscosity of monomer, Poise	$\eta_o = 1.98 \times 10^{-4} + 1.15 \times 10^2 T^{-2}$	(30)
Prandtl Number	$Pr = \eta_s C_p / K$	(31)
Heat transfer coefficient for metal wall (cal/cm ² .s.K)	$h_w = 0.025$	(32)

Initiation of radicals are important process that promotes polymerization [8]. Curve number 1 demonstrates a much delayed reaction process. As soon as the reacting mixture (lower temperature) introduced into the reactor, it is heated by jacket fluid up to the optimal temperature for initiator decomposition and it is time consuming, therefore the reaction took place much later in the reactor axial length. The highest temperature peak is recorded at temperature of 231.46°C obtained by curve number 3, where the disparity from another two curves is merely $\pm 10^\circ\text{C}$ and can be considered as insignificant. From this study it is observed that the kinetic constant value of monomer thermal initiation is extremely small, therefore its inclusion in this model does not give any significant effect in the temperature peak.

In Figure 2 (b), monomer conversion (%) profiles also demonstrate a sudden jump at the same location, corresponding to the temperature peak in Figure 2 (a). Initiator introduced in the reactor, depleted immediately after its introduction into the reactor. As the reaction temperature reach its highest peak, it is observed that the reactor temperature profile dropping down immediately, indicating that all of the initiators are exhausted and no further reaction occur from this point onwards. In Figure 2 (b), the highest monomer conversion is 26.44% obtained by curve number 1, followed by curve number 2 and number 3 at 23.19% and 19.55%. It is believed that the effect of feed temperature become significant to ensure the maximum utilization of initiator. Typically peroxides, which are used as common industrial initiator, have their own half-life temperature ranges. Under thermal condition, peroxides exhibit dissimilar rates of decomposition depending to their half-life temperatures. In curve number 3, the feed temperature is higher from curve number 1 feed temperature by 40°C and due to this fact; few amount of the initiator might not decompose or in other words might not turn into radicals, thus reducing the monomer conversion percentage.

Table 3. Rate constants and parameters used in this study

	Rate of reaction constant (1/s)	Source
Rate constant of monomer thermal initiation, K_{th}	$4.0E11 \exp[-1.982E4(T + 273.15)^{-1}]$	[11]
Rate constant of propagation, K_p	$9.9E5 \exp[-2.1185E3(T + 273.15)^{-1}]$	[11]
Rate constant of termination by combination, K_{tc}	$4.4E4 \exp[-2.06E3(T + 273.15)^{-1}]$	[9]
Rate constant of chain transfer to monomer, K_{tm}	$1.2E5 \exp[-7.2461E3(T + 273.15)^{-1}]$	[11]
Rate constant of chain transfer to polymer, K_{tp}	$1.8E8 \exp[-4.7303E3(T + 273.15)^{-1}]$	[11]
Rate constant of β -scission to secondary radical, K_{β}	$1.4E9 \exp[-9.6114E3(T + 273.15)^{-1}]$	[11]
Rate constant of β -scission to tertiary radical, $K_{\beta 1}$	$4.4E9 \exp[-9.6114E3(T + 273.15)^{-1}]$	[11]
Rate constant of termination by thermal degradation, K_{thd}	$7.7E4 \exp[-9.618E3(T + 273.15)^{-1}]$	[3]
Rate constant of chain transfer to solvent, K_{ts}	$5.6E7 \exp[-5.0484E3(T + 273.15)^{-1}]$	[11]
Rate constant of peroxide initiation, K_d	$2.3E13 \exp[-1.5163E4(T + 273.15)^{-1}]$	[12]
Parameters		
Tubular reactor length, L (m)	1200	
Reactor diameter, D (m)	0.05	
Pressure, P (atm)	2000	
Initial concentration of monomer, C_{M0} (mol/l)	19.54	
Initial concentration of initiator, C_{I0} (mol/l)	1.5E-3	
Initial reaction mixture velocity, v_0 (m/s)	18.8	
Feed Temperature, T_F ($^{\circ}$ C)	120, 140, 160	
Jacket Temperature, T_J ($^{\circ}$ C)	180	

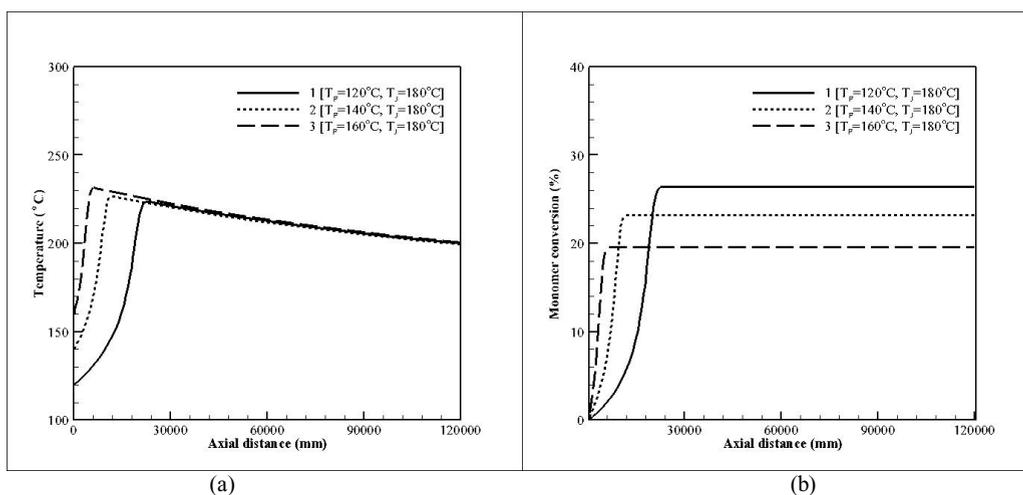


Fig. 2: (a) Reactor temperature profile with regards to its axial distance (b) Axial variation of monomer conversion

4. Conclusion

The simulation of tubular LDPE reactors with single feed and injection point has been performed. Selective reaction mechanisms with reliable rate constants were used for the present study. The results obtained in this study were in good agreement and acceptable to the range of those substantial researches. The present study reveals that the effect of feed temperature is significant as it contributes to monomer conversion percentage. This finding motivates for the solution of sophisticated optimal temperature control with the goal to maximize the monomer conversion.

Acknowledgements

The authors gratefully acknowledge the financial support given by Universiti Sains Malaysia through Research University Grant No. 1001/PJKIMIA/814237 and Malaysian government through MyBrain 15 funding.

Nomenclature

A_c	Cross-sectional area of tubular, m^2
C_{Im}	concentration of initiator, mol/l
C_M	monomer concentration, mol/l
C_S	solvent concentration, mol/l
C_p	specific heat of reactant mixture, cal/g·K
D	inside diameter of reactor, cm
f	efficiency of original initiation
h_i	reactor side heat transfer coefficient, $cal/m^2 \cdot s \cdot K$
h_w	heat transfer coefficient for metal wall, reactor jacket, & fouling, $cal/m^2 \cdot s \cdot K$
I	initiator
K_d	rate constant of peroxide initiation, l/s
K_{th}	rate constant of monomer thermal initiation, l/s
K_p	rate constant of propagation, $l/mol \cdot s$
K_{td}	rate constant of termination by thermal degradation, $l/mol \cdot s$
K_{thd}	rate constant of termination by disproportionation, $l/mol \cdot s$
K_{trm}	rate constant of chain transfer to monomer, $l/mol \cdot s$
K_{trp}	rate constant of chain transfer to polymer, $l/mol \cdot s$
K_{trs}	rate constant of chain transfer to solvent, l/s
K_β	rate constant of β -scission to secondary radical, l/s
$K_{\beta t}$	rate constant of β -scission to tertiary radical, l/s
K	thermal conductivity
L	length of reactor, m
M	monomer
Nu	Nusselt number
P	reaction pressure, atm
Pr	Prandtl number
P_l	dead polymer with chain length l
P_k	dead polymer with chain length k
R_{in}	primary initiator radical
R_l	radical of chain length l
R_k	radical of chain length k
Re	Reynolds number
S	solvent
T	temperature of reactants (or reactor), °C
T_J	temperature of reactor jacket (or its fluid), °C
U	overall heat transfer coefficient, $cal/m^2 \cdot s \cdot K$
v	axial velocity of reactant mixture, m/s
V_P	specific volume of polymer, cm^3/g
V_M	specific volume of monomer, cm^3/g
w_m	weight fraction of monomer
w_p	weight fraction of polymer
z	axial distance from reactor inlet, m

Greek Symbols

λ_i	i-th moment of live polymer radical
$-\Delta H$	heat of reaction, cal/mol
ρ	reaction mixture density, g/cm ³
η_s	viscosity of reactant mixture, Poise
η_r	relative viscosity of monomer
η_o	viscosity of monomer, Poise
μ_i	i-th moment of dead polymer

References

- [1] A. Azmi and N. Aziz, Low Density Polyethylene Tubular Reactor Modeling: Model Developments and Future Directions, 28th Symposium of Malaysian Chemical Engineers (2015) 352-360.
- [2] D.M. Kim, & P.D. Iedema, Modeling of branching density and branching distribution in low-density polyethylene polymerization. Chemical Engineering Science. 63 (2008) 2035 – 2046.
- [3] N. Agrawal, G.P. Rangaiah, A.K. Ray and S.K. Gupta, Design Stage Optimization of an Industrial Low Density Polyethylene Tubular Reactor for Multiple Objectives Using NSGA-II and Its Jumping Gene Adaptations. Chemical Engineering Science. 62 (2007) 2346 – 2365.
- [4] C. Kiparissides, A. Baltas, S. Papadopoulos, J.P. Congalidis, J.R. Richards, M.B. Kelly, and Y. Ye, Mathematical Modeling of Free-Radical Ethylene Copolymerization in High-Pressure Tubular Reactors. Ind. Eng. Chem. Res. 44 (2005) 2592 – 2605.
- [5] C.H. Chen, J.G. Vermeychuk, J.A. Howell, and P. Ehrlich, Computer Model for Tubular High-Pressure Polyethylene Reactors. AIChE J. 22 (1976) 463 – 471.
- [6] K. Gupta, A. Kumar, and M.V.G. Krishnamurthy, Simulation of Tubular Low-Density Polyethylene. Polym. Eng. Sci. 25 (1985) 37-47.
- [7] M. Asteasuain, S. Pereda, M.H. Lacunza, P.E. Ugrin, and A. Brandolin, Industrial high pressure ethylene polymerization initiated by peroxide mixtures: A reduced mathematical model for parameter adjustment. Polymer Engineering and Science. 41 (2001) 711–726.
- [8] F.Z. Yao, S.R. Upreti, A. Lohi, and R. Dhib, Modeling, Simulation and Optimal Control of Ethylene Polymerization in Non-Isothermal, High-Pressure Tubular Reactors. International Journal of Chemical Reactor Engineering. 2 (2004) 1542 – 6580.
- [9] G. Donati, M. Marini, L. Marziano, C. Mazzaferrri, M. Spampinato, and E. Langianni, Mathematical-Model of Low-Density Polyethylene Tubular Reactor. Chemical Reaction Engineering. 196 (1982) 579–590.
- [10] P. Ehrlich and G.A. Mortimer, Fundamentals of the Free Radical Polymerization of Ethylene. Adv. Polym. Sci. 7 (1970) 386 – 448.
- [11] F.Z. Yao, Modeling, Simulation and Optimal Control of Ethylene Polymerization in a High-Pressure Tubular Reactor, Master's thesis, Department of Chemical Engineering, Ryerson University, Toronto (2003).
- [12] S. Agrawal and C.D. Han, Analysis of High-Pressure Polyethylene Tubular Reactor with Axial Mixing. AIChEJ. 21 (1975) 449 - 465.