Effect of initiator concentration to low-density polyethylene production in a tubular reactor

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Abstract. Low-density polyethylene (LDPE) is one of the most widely used polymers in the world, which is produced in high-capacity tubular and autoclave reactors. As the LDPE industry turn into more competitive and its market profit margins become tighter, manufacturers have to develop solutions to debottleneck the reactor output while abiding to the stringent product specification. A single polyolefin plant producing ten to forty grades of LDPE with various melt flow index (MFI), therefore understanding the reaction mechanism, the operating conditions as well as the dynamic behavior of tubular reactor is essential before any improvement can take place. In the present work, a steady state mathematical model representing a tubular reactor for the production of LDPE is simulated using MATLAB R2015a®. The model developed is a function of feed inlet, reactor jacket, single initiator injector and outlet stream. Analysis on the effect of initiator concentration (CI) shows sudden declining trend of initiator's concentration which indicates that all of the initiators are exhausted after polymerization reaction and no further reaction occur from this point onwards. Furthermore, the results demonstrate that the concentration of initiator gives significant impact on reactor temperature's profile and monomer conversion rate, since higher initiator concentration promotes greater polymerization rate, and therefore leads to higher monomer conversion throughput.

1.   Introduction

LDPE is one of the most important commodity polymer with great industrial significance. The LDPE is known to be possessing extraordinary electrical and impact properties, and excellent resistance to chemical and moisture. Globally, LDPE is widely used for manufacturing various plastic containers, plastic packaging for computer hardware, dispensing bottles, tubing, and various molded laboratory equipment. Nevertheless, its most common use is still in plastic bags. Due to its exclusive properties, LPDE worldwide consumption has been reported to increase. The global LDPE production reached over 35 million metric tons in 1994, and has been reported to growth rapidly at the proportion of 7% per year over the past 15 years [1-2].

The high-pressure polymerization of ethylene in tubular reactors is broadly employed to produce LDPE. The free radical polymerization in a tubular reactor is carried out under extreme conditions. The reactor is operated at very high pressure, typically between 150 – 250 MPa and temperatures of 325 – 625 K [3]. A typical high-pressure LDPE tubular reactor's length is ranging from 500 to 1500 m and characterized by very large ratios of length to diameter (L/D) from $1 – 6 \times 10^4$. Schematic diagram of a typical industrial LDPE tubular reactor is shown in Figure 1. Ethylene (monomer), transfer agents along with initiators are used as the reactor feed. Ethylene polymerization is a highly exothermic reaction and it takes place in short reaction zones resulting from peroxides injections. The remainder of the reactor is mainly used as heat exchanger, where the reaction mixture is heated up or cooled down to an appropriate temperature for subsequent peroxide addition or downstream process.

Considering the extreme operating conditions and the complexity of ethylene polymerization process, it is apparently known that there are difficulties to obtain good model formulation of the process. An accomplished model should be able to maximize the monomer conversion, minimizing the unwanted product (ethyl, butyl, vinyl and vinylidene groups); while abiding to the stringent

polymer product quality with regards to its molecular weight distribution (MWD). However, to achieve all objective functions at one time will be very exhausting, therefore a divide and conquer strategy is adopted in the present work. Here, the effect of initiator concentration variations on reactor temperature profile and ethylene conversion across the tubular reactor is evaluated with the improvement in kinetic scheme used by Yao et al. [1] and Gupta et al. [4] models. It is believed that the results obtained will allow significant improvements in conversion of ethylene.
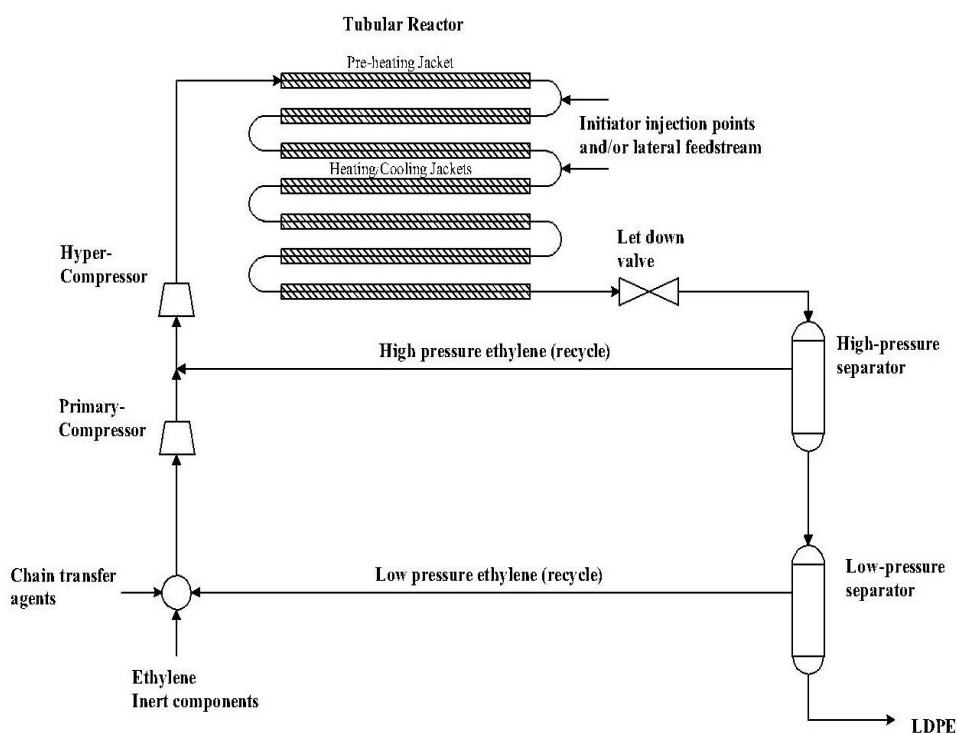

Figure 1. Simplified flowsheet of LDPE plant

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)

Table 2. Model Equations for the LDPE Tubular Reactor

Descriptions	Equation	Equation
Overall mass balance	$\dfrac{dv}{dz} = -\dfrac{v}{\rho}\left(\dfrac{d\rho}{dz}\right)$	(11)
Initiator balance	$v\dfrac{dC_{I_m}}{dz} = \left(-2fK_{d_m}C_{I_m} - C_{I_m}\dfrac{dv}{dz}\right) \therefore for\ m = 1,2$	(12)
Monomer balance	$v\dfrac{dC_M}{dz} = \left(2K_{th}C_M{}^3 - K_{trm}C_M\lambda_0 - C_M\dfrac{dv}{dz}\right)$	(13)
Solvent balance	$v\dfrac{dC_S}{dz} = \left(-K_{trs}C_S\lambda_0 - C_S\dfrac{dv}{dz}\right)$	(14)
Reactor temperature	$\dfrac{dT}{dz} = \dfrac{1}{\rho C_P v}\left[-\Delta H K_p C_M \lambda_{00} - \dfrac{4U(T-T_J)}{D}\right]$	(15)
Reaction mixture density variation	$\dfrac{d\rho}{dz} = \dfrac{\partial\rho}{\partial T}\dfrac{dT}{dz} + \dfrac{\partial\rho}{\partial C_M}\dfrac{\partial C_M}{dz}$	(16)

where (17)

$$\frac{\partial\rho}{\partial T} = \frac{1.436 \times 10^{-6}C_M - 2.5245 \times 10^{-4} + (31.6967 - 1.25C_M) \times 10^{-8}T - 9.98877 \times 10^{-11}T^2}{(0.71 - 4.475 \times 10^{-4}T)^2(0.949 + 4.988 \times 10^{-4}T)^2}$$

and (18)

$$\frac{\partial\rho}{\partial C_M} = 0.028\left(\frac{1 - 0.71 - 4.475 \times 10^{-4}T}{0.949 + 4.988 \times 10^{-4}T}\right)$$

Descriptions	Equation	Equation
Overall heat transfer coefficient	$U^{-1} = h_i^{-1} + h_w^{-1}$	(19)
Reaction mixture density (g/cm^3)	$\rho = \dfrac{1 + 0.028C_M(V_P - V_M)}{V_P}$	(20)
Specific heat of reactant mixture (cal/g.K)	$C_p = 0.518w_m + (1.041 + 8.3 \times 10^{-4})w_p$	(21)
Heat of reaction (cal/mol)	$-\Delta H = 23000$	(22)
Moment of live polymer radical	$\lambda_0 = \sqrt{\dfrac{2fK_{d_m}C_{I_m} + 2K_{th}C_M{}^3}{K_{tc}}}$	(23)
Reactor side heat transfer coefficient (cal/cm^2.s.K)	$h_i = \dfrac{K(Nu)}{D_i}$	(24)
Thermal conductivity (cal/cm.s.K)	$K = (5w_m + 3.5w_p) \times 10^{-4}$	(25)
Nusselt Number	$Nu = 0.026Re^{0.8}Pr^{0.33}$	(26)
Reynolds Number	$Re = \dfrac{\rho D_i v}{A_c \eta_s}$	(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)

2.   Model formulation
2.1. Assumption
The reactor model is based on the following assumptions:
- Ideal plug flow assumption with no axial mixing [1,4-5]

- The pressure inside reactor is kept constant throughout the reactor since the pressure drop of each zones are less than 10%, which is insignificant [3]
- There is no pulse valve effect in the model as inferred from pilot plant studies by Donati et al. [7]
- Homogenous phase of reaction mixture is assumed as suggested by Ehrlich and Mortimer [11]
- The heat capacity of reaction mixture is denoted as total heat capacities of pure components as prescribed by Chen et al. [5]
- 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.
- Volumetric flow rate and temperature of jacket fluid is kept constant [1,5]
- Ten reaction mechanism is chosen and listed in Table 1
- Single feed and initiator injection point where the axial location of feed and initiator, $z = 0.0$ mm

2.2. Simulation

The developed model consist of ODEs, are solved using MATLAB R2015a®. The differential equations have been solved using ode23solver due to its suitability for stiff differential equations, furthermore it is a variable order solver based on the numerical differentiation formulas (NDFs). The reaction mechanisms, reaction rate constants, design features and operating conditions for based case, are given in Tables 1 - 3. Equations 1 – 10 list all the reaction mechanisms chosen in this study. Equations 11 – 14 constitute the mass balance on each components in the reactor, whereas Equation 15 represents the heat transfer from the reaction mixture to the jacket coolants. The density variation was present in Equation 16 – 18 followed by the physical properties of the reaction mixture and tubular reactor which are described in the Equations 19 – 32.

Table 3. Rate constants and parameters used in this study

Rate of reaction constant (1/s)		Source
Monomer thermal initiation, K_{th}	$6.04E3 \exp [-36.707E3(T + 273.15)^{-1}]$	[8]
Propagation, K_p	$9.9E5 \exp [-1.982E3(T + 273.15)^{-1}]$	[8]
Termination by combination, K_{tc}	$4.4E4 \exp [-3.772E2(T + 273.15)^{-1}]$	[7]
Chain transfer to monomer, K_{trm}	$1.2E5 \exp [-6.758E3(T + 273.15)^{-1}]$	[8]
Chain transfer to polymer, K_{trp}	$1.8E8 \exp [-4.7303E3(T + 273.15)^{-1}]$	[8]
β-scission to sec. radical, K_{β}	$1.4E9 \exp [-9.371E3(T + 273.15)^{-1}]$	[8]
β-scission to tertiary radical, $K_{\beta I}$	$4.4E9 \exp [-9.371E3(T + 273.15)^{-1}]$	[8]
Thermal degradation, K_{td}	$7.7E4 \exp [-9.618E3(T + 273.15)^{-1}]$	[9]
Chain transfer to solvent, K_{trs}	$5.6E7 \exp [-5.29E3(T + 273.15)^{-1}]$	[8]
Peroxide initiation, K_d	$6.5E11 \exp [-1.28E4(T + 273.15)^{-1}]$	[10]
Parameters		
Tubular reactor length, L (m)	1200	
Reactor diameter, D (m)	0.05	
Pressure, P (atm)	2000	
Initial concentration of monomer,	19.54	
Initial concentration of initiator,	1.5E-3, 3.0E-3, 4.5E-3	
Initial reaction mixture velocity, v_o (m/s)	18.8	
Feed Temperature, T_F (^{o}C)	140	
Jacket Temperature, T_J (^{o}C)	180	

3.   Results and Discussions

The simulation of the model are solved in MATLAB R2015a® and the results are presented in the Figures. 2 – 5. The initiator concentration (CI) of 1.5 x 10^{-6}mol/cm^3, ethylene concentration (CM) of 19.54 x 10^{-3}mol/cm^3, reaction mixture velocity of 18.8 m/s, tube length of 1200 m, reactor inner diameter of 0.05 m, feed temperature of 140°C and constant reactor pressure of 2000 atm are chosen as the reference condition in this simulation. Table 2 list out almost all parameters which are applied in this work. Temperature profiles and monomer conversion across the tubular reactor are selected as dependent variables for this particular analysis.

Figure 2 shows the temperature profiles within the reactor. It can be observed that reactor temperature rises sharply to a peak value in the 0 to 15000 mm axial range. For CI of reference condition, the peak value is observed at $z = 12030$ mm, whereas for CI of 3.0 x 10^{-6}mol/cm^3 and 4.50 x 10^{-6}mol/cm^3, the ethylene conversions are 27.05% and 29.34%, respectively. Judging from Figure 2 and Figure 3, both reactor temperature and ethylene conversion profiles are observed to be in agreement to one another. This is true since higher initiator concentration promotes greater ethylene conversion and therefore increasing the peak temperature. This is due to exothermic nature of ethylene polymerization.

As the reaction temperature achieve its highest peak, conversion of ethylene become static indicating that no further reaction take place from this point forwards. This is due to the initiator depletion rapidly to zero after its introduction in the tubular reactor as seen in Figure 4. As a result, concentration of monomer become constant from this point until the reactor outlet. From Figure 4, it is noticeable that 100% of initiator had been consumed during the reaction, whereas for monomer there is some remaining amount left even after the process is completed as seen in Figure 5. The final concentration for CI of 1.5 x 10^{-6} (reference condition), 3.0 x 10-6 mol/cm^3 and 4.50 x 10^{-6} mol/cm^3 are 15 x 10^{-3} mol/cm^3, 14.25 x 10^{-3} mol/cm^3 and 13.81 x 10^{-3} mol/cm^3 respectively.
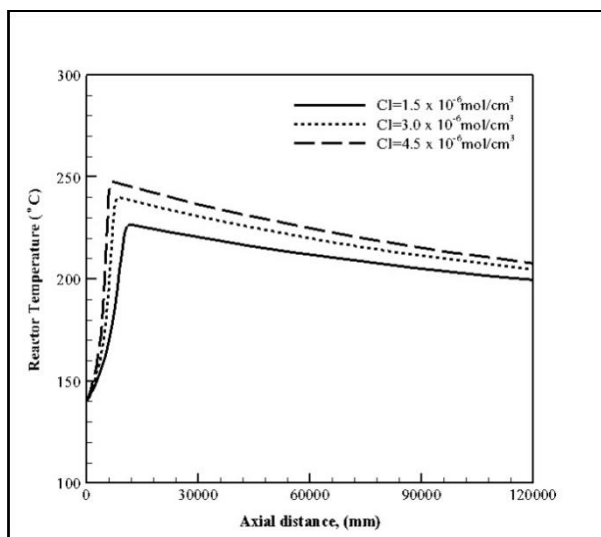

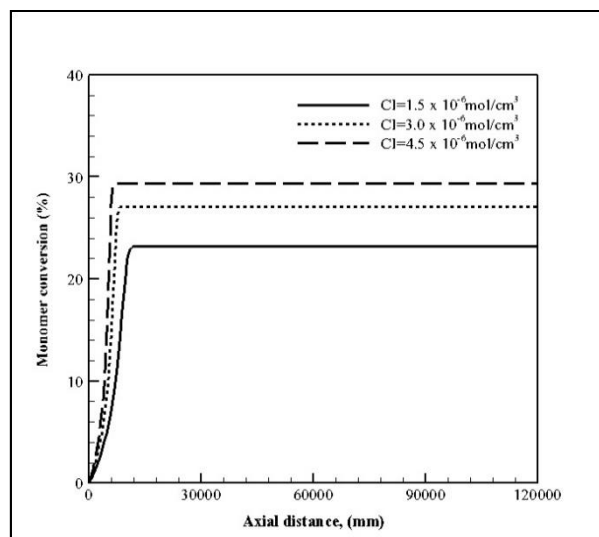**Figure 2.** Reactor temperature profiles along reactor length

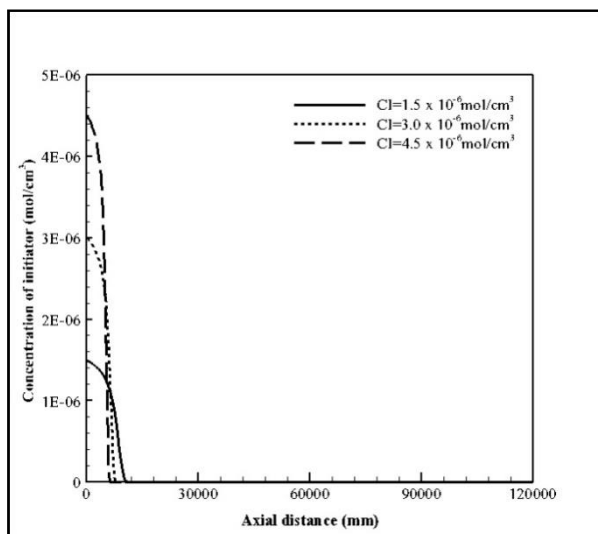**Figure 3.** Monomer conversions along reactor length

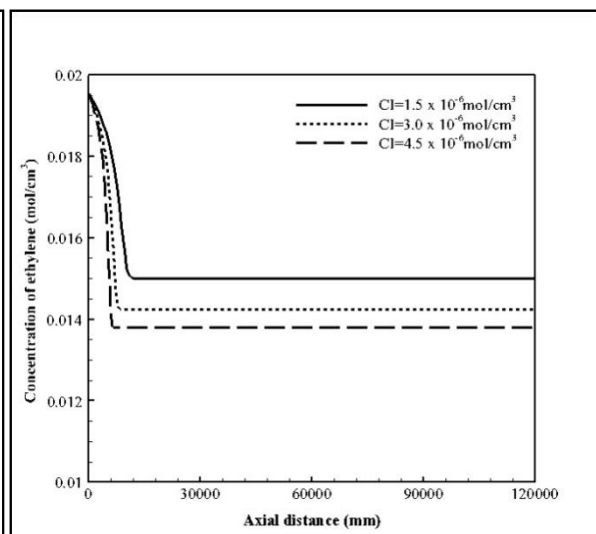| **Figure 4.** Concentration of initiators along reactor length | **Figure 5.** Concentration of monomers along reactor length |

4. Conclusion

The simulation of high pressure LDPE production has been carried out using selected reaction mechanism and kinetic constant from various literature sources. The present study reveals that initiator concentration amount plays significant role to the ethylene conversion rate. Higher initiator concentration leading to a higher concentrations of free radical and thus increasing the ethylene conversion rate. In the future, it will be very beneficial to conduct a comparison study of varying the amount of initiator versus adding extra injector to a LDPE tubular reactor.

Nomenclature

Ac	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
I	initiator
M	monomer
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

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