

Modeling and Simulation of Low Density Polyethylene (LDPE) High Pressure Tubular Reactor

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Abstract

Low Density Polyethylene (LDPE) is produced by free radical polymerization. Industrially, LDPE polymerization process is usually carried out in a continuous mode (tubular or autoclave reactors) at high pressures (1300-3400 atm) and temperatures (50-340 °C). LDPE exhibits a number of desirable properties, including high tensile strength, flexibility, high impact resistance, low crystallinity, low density, high resistance to solvents, chemicals, and oxidating agents. In the present study, existing mathematical model for LDPE process is improved by tuning the model parameters. This model consists of mass, momentum and energy balance equations along with reaction kinetic equations and property correlations totalling to 25 coupled, nonlinear and highly stiff differential equations. The mathematical models comprise of a set of 13 model parameters (including activation energies for 8 reactions, volumetric flow rate of 4 jackets and a constant used in viscosity estimation), which are tuned by minimizing the sum-of-squares of the normalized error, between the model-predicted and the actual experimental values obtained from industry using a population based search algorithm named Differential Evolution (DE). The model is simulated using ODE15s (Gears technique) routine of MATLAB. The model predicted results are compared with the data available in the literature and the industrial data. Such model is useful in analysing the process plant by further carrying out multi-objective optimization study considering different sets of conflicting objectives.

INTRODUCTION

Since past more than 30 years several mathematical models have been developed and simulated for high pressure low density polyethylene (LDPE) reactor with varying degrees of configuration. Industrially polyethylene (PE) is produced by both high pressure (free radical) and low pressure (ionic addition) ethylene process. Two kinds of reactor configurations are employed in high pressure free radical production process; those are tubular technology and multi impeller stirred autoclave technology.

The quality of PE mainly depends on density and degree of branching. Depending upon the density, the PE can be classified into LDPE ($0.91\text{-}0.925\text{ kg/m}^3$), medium density polyethylene (MDPE) ($0.926\text{-}0.94\text{ kg/m}^3$) and high density polyethylene (HDPE) ($0.941\text{-}0.965\text{ kg/m}^3$). The density of PE is also related to the degree of short chain branching (SCB). The higher the degree of SCB, the lower is the density of PE. In LDPE, typically 10-40 SCB and 0.3-03 long chain branching (LCB) exists respectively per thousand backbone carbon atoms. The model used in the present study is based on well known and widely accepted kinetic scheme for free radical polymerization of ethylene to polyethylene. The model includes the reaction schemes such as initiation, propagation, termination by various mechanisms such as by combination, by thermal degradation, by chain transfer to monomer and by chain transfer to the solvent. Second order moment equations are used to define the concentration of growing and dead polymer species. The mathematical models comprises of 25 numbers of coupled nonlinear and highly stiff differential equations and property correlations. Heat balance is simulated by considering constant temperature of the coolant on the shell side. The stiffness in the differential equation is due to wide variation in the rates of various species involved in the overall reaction scheme. Physical properties of the reaction mixture such as density, viscosity and thermal conductivity are assumed to vary along the reactor length.

Due to the increased demand and in order to improve the performance of LDPE production process, several studies are reported in the literature on modeling and simulation of polyethylene. Agarwal and Han [1] focused on axial mixing analysis of tubular reactor by incorporating the axial mixing parameter, the Peclet number. They studied effects of various operating parameters such as feed conditions, axial mixing, and chain transfer to dead polymers etc. on the reactor performance. However, Chen et al. [2], in their study, summarized not to include axial mixing due to high value of Peclet number and excessive turbulence. Gupta et al. [3] carried out simulation of tubular LDPE reactor with intermediate feeds. Effects of various operating parameters such as jacket temperature, feed temperature, initiator concentration, wall heat transfer coefficients and reactor diameter was tested on the reactor performance. It was concluded that reactor operation becomes inherently unstable under certain operating conditions. Shirodkar and Taien [4] presented a mathematical model for tubular reactor and compared the performance of model with actual plant data. Brandoline et al. [5] proposed a mathematical model for high pressure polymerization of ethylene in tubular reactor. Kinetic parameters were determined by non linear regression analysis based on measured reaction temperature and molecular weight distribution properties. The model proposed by this group gave model predictions in agreement with the industrial data in the range with certain

degree of error. Katz and Siedel [6] presented a comprehensive method of moments for representing size distribution of free radical polymerization. Lee et al. [7] studied decomposition phenomena in an industrial high pressure autoclave polyethylene reactor.

Kalyon et al. [8] made a simulation based study of high pressure polymerization of ethylene and its rheological behavior. Data from commercial reactor was used having a reactor length of 720 m. Model predictions and experimental properties for the long and the short chain branching for three different polyethylene resin was obtained in their study. Rheological behavior of three different resins was studied with respect to apparent viscosity, shear stress, modulus of elasticity etc. More recently Kim and Iedema [9] carried out modeling of the branching density and the branching distribution in the low density polyethylene polymerization. They concluded that the concentration of long chain branching (LCB) are close to those of first branching moments in both the CSTR and the tubular reactor systems.

SIMULATION AND OPTIMIZATION

Brandoline et al. [10] presented a comprehensive model which proved to be a well known model which included several mechanisms of termination reactions. They also included the effect of the pulse valve in their study. Agarwal et al. [11] made use of model proposed by Brandoline et al. [10]. They carried out the tuning of important rate parameters involved in the model. When we tried to use the model predicted parameters reported by Agarwal et al.[11], we observed a slight deviation in the exit concentrations of various species. However, the trend followed by each species remains same, as reported in the literature [10, 11]. ODE15s routine of Matlab library is used in present study. ODE15s in MATLAB 7.0 library is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally it uses backward differentiation formula (BDFs, also known as Gears method) that is usually less efficient. For sufficiently small step size, NDF can achieve the same accuracy as BDF with step size about 26% bigger. [12]. Agarwal et al. [11] used the Gears Routine (D02EJF of NAG library) in their simulation runs.

The slight deviation in the in the exit concentration of various species encouraged us to fine tune the model in order to find the rate law parameters associated with the several reactions. A complete set of 13 model parameters used to fine tune used for model equation is available in literature [11]. The Differential Evolution (DE) algorithm [13, 14, 15] is used to minimize the sum of square of the normalized error, I , between the model-predicted values and the industrial values (Eq. 1),

$$\text{Minimize } I(\mathbf{u}) = \sum_{i,j} \left(1 - \frac{N_i^{\text{ind}}(x_j)}{N_i^{\text{m}}(x_j)_t} \right) \quad \text{----- (1)}$$

where, N_i stands for the value of the i^{th} property, and the superscripts m and “ind” represent the values predicted by the model and the industrial values, respectively. Properties used in the estimation of function I in this study are temperature of reactor, number average molecular weight, monomer conversion and methyl, vinyl and vinylidene end groups / 1000 carbon atoms in the chain. The decision variables involved in this study are given by given by Eq. 2

$$I(\mathbf{u}) \cong f((E_0, E_{d1}, E_{d2}, E_p, E_{trs}, E_{bb}, E_{b1}, E_b, V_{j2}, V_{j3}, V_{j4}, V_{j5}, \alpha_v) \quad \text{----- (2)}$$

RESULTS AND DISCUSSION

Fig. 1 shows the schematic of 5 zone industrial LDPE tubular reactor. The total length of reactor considered in this study is 1390 m with inside diameter of 0.05 m. The entire length of the reactor is divided into 5 zones and the length of each zone is 60, 100, 180, 510, and 540 m respectively. Constant jacket temperature is assumed in each zone. Ideal plug flow conditions are assumed in the reactor and jacket sides. The reaction mixture is assumed to be homogeneous. 25 sets of non-linear coupled differential equations, describing mass, energy and momentum balance are integrated using ODE15S routine in Matlab library. The monomer (ethylene), solvent (telogen), inert (n-butane) and oxygen are fed at the inlet of the reactor. First two zones of the reactor acts as a heating zones and no reaction occurs in these zone. All reactions are assumed to be elementary except oxygen initiation reaction, where reaction is considered to be of order 1.1, with respect to oxygen [5]. Initiator I_1 (tert-butyl peroxyvalate) is injected at the entrance of 3rd zone while initiator I_2 (tert-butyl, 3,5,5 trimethyl peroxyhexaonate) is injected at the entrance of 5th zone [11].

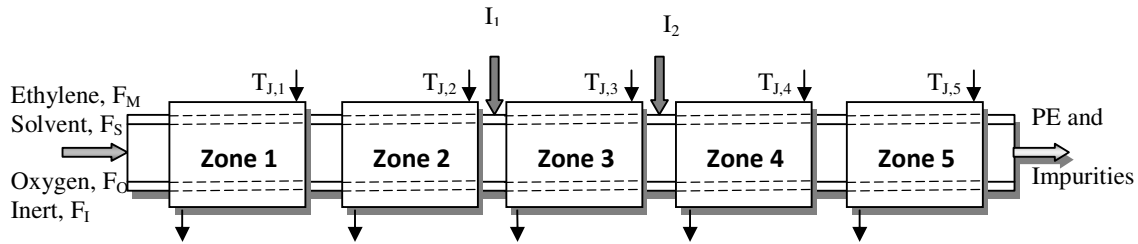


Figure 1: Schematic flow diagram of 5 zone LDPE tubular reactor

The bounds and the values of optimal parameters obtained in different studies and the results obtained in present study are reported in Table 1. Our study using DE resulted in several near optimal solutions, each solution among these near optimal solution resulted the same cost value up to the order of 10^{-4} . Due to these equally good optimal solutions, we selected randomly a set of solutions which is reported in Table 1. Brandoline et al. [10] did not provide the actual values of the activation energies of peroxide initiator (d_1 and d_2) due to commercial agreement. However, they reported the bounds of those variables. We used the same bounds of these variables in the present study. The bounds of decision variables used in present study are kept same as that of reported in the literature [11]. Fig. 2 (a) shows the monomer conversion profiles. Monomer conversion shoots up to an intermediate level at the initiator 1 injection point. Fig. 2 (b) shows the temperature profile plotted along with the monomer conversion. The initiation reaction is highly exothermic in nature which raises the reactor temperature. It is important to control the temperature of reactor by controlling the initial monomer and initiator concentration. After the first peak of monomer

conversion, the reactor mixture is allowed to cool before the second injection takes place. The injection of second initiator again raises the temperature of reactor and monomer conversion to its highest achievable limit. No further increase in monomer conversion is observed beyond this point.

Table 1: Bounds and values of optimal parameters obtained in different studies

Bounds of variables	Reported Values [10]	Reported Values [11]	Obtained Values Present study
$125604 < E_0 < 138164$	135945	132168	133232.3212
$117230 < E_{d1} < 136071$	94621-133140	119929	123702.3529
$117230 < E_{d2} < 133977$	94621-132721	123117	127803.8755
$14653 < E_p < 18003$	17626	17431	18002.74517
$14653 < E_{trs} < 20934$	17253	18406	20927.265
$56521 < E_{bb} < 66988$	61964	60537	60832.98655
$71175 < E_{b1} < 87922$	79967	84747	79828.44094
$62802 < E_b < 87922$	79967	70205	76149.3458
$0.005 < V_{j2} < 0.007$	0.0012	0.00403	0.00690141
$0.005 < V_{j3} < 0.007$	0.0012	0.00394	0.00634553
$0.005 < V_{j4} < 0.007$	0.0012	0.00332	0.00167684
$0.001 < V_{j5} < 0.005$	0.0012	0.00022	0.00125074
$0.009 < a_v < 0.0185$	0.017	0.018	0.0132271

Fig 3 (a) & (b) shows the profiles of SCB/1000 C atoms and the vinyl group/1000 C atoms respectively along the reactor length. Short chain branching depends on the highest temperature attained in the reactor. The first peak in temperature is responsible for the sharp increase in the SCB concentration and the vinyl end group concentration. Fig. 4 (a) and (b) shows the profiles of vinylidene group/1000 C atoms and the number average molecular weight along the reactor length. Analysis Figs. 2, 3 and 4, reveals that the attainment of highest temperature marks the depletion of the initiator concentration. Thereafter, monomer conversion also ceases and the SCB, vinyl, vinylidene concentration and the number average molecular weight values of the product stream remain constant until the second initiator is made available at initiator 2 injection point. Physically not much change takes place in the reactor after the attainment of highest temperature except for the cooling of the material flowing within the reactor.

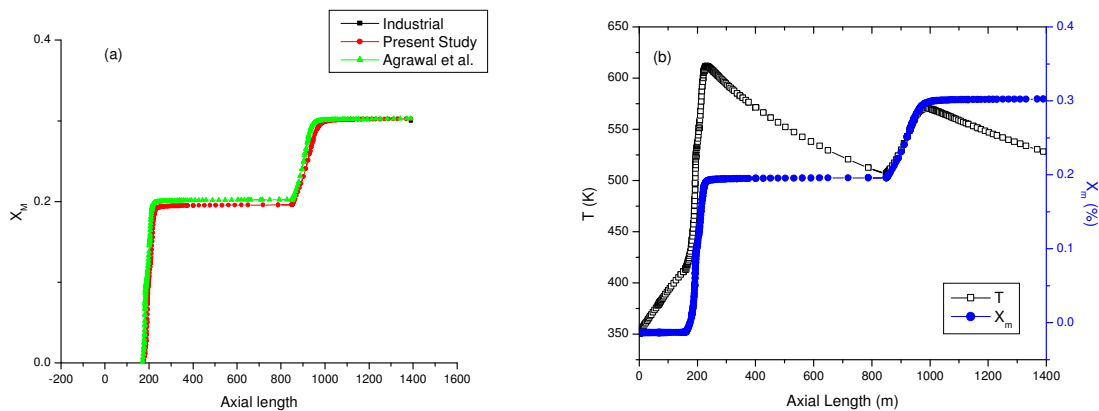


Figure 2: (a) Monomer conversion profile; and (b) profiles of temperature and monomer conversion

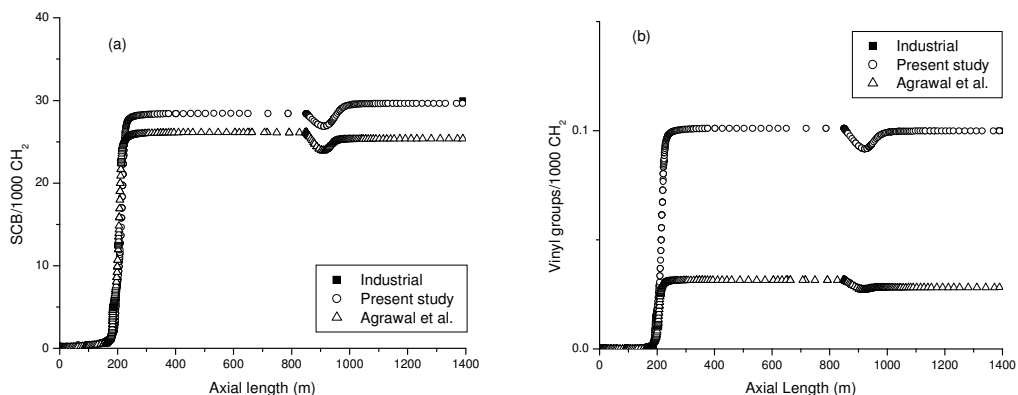


Figure 3: (a) SCB/1000 C atoms; and (b) vinyl group/1000 C atoms profile along the reactor length

CONCLUSIONS

The parametric optimization and simulation of low density polyethylene tubular reactor is carried out using evolutionary differential evolution optimization technique. The physical properties and the pressure, temperature and several main and side chain concentrations are assumed to vary along the reactor length. The present study results reveal that the operation of LDPE tubular reactor depends upon several parameters. The estimation of correct reaction rate parameters can help in predicting the output of a process especially in the presence of uncertain initial concentrations and the reactor operating conditions. The detailed stability analysis of the reactor emphasising on varied feed concentrations, jacket temperatures, change in diameter and the change in the initiator concentration and the injection position can lead to a better analysis of the reactor system.

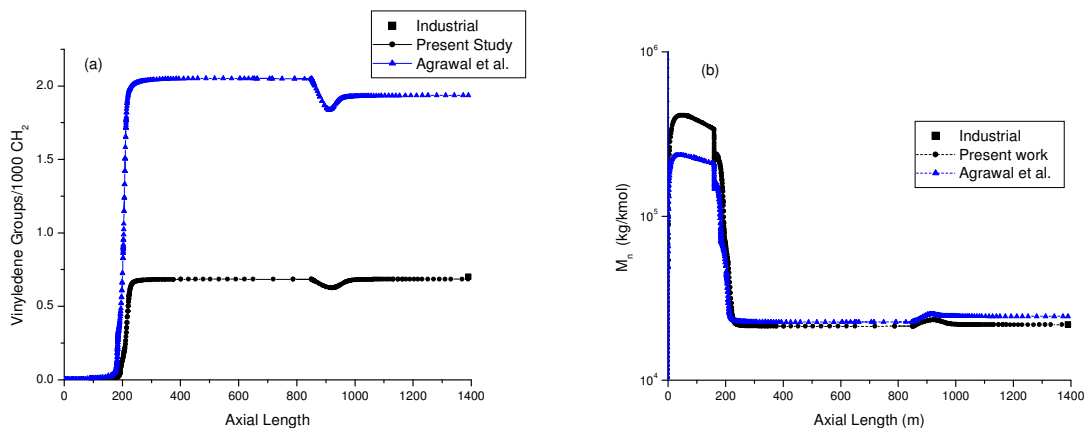


Figure 4: (a) Vinylidene end group/1000 C atoms; and (b) M_n profile along the reactor length

Nomenclature

N_i i^{th} property used in the simulation
 E activation energy
 SCB short chain branching

Superscripts and Subscripts

ind industrial
 m model predicted
 b β -scission of tertiary radical
 b1 β -scission of secondary radical
 bb backbiting (intra-molecular chain transfer)
 d_1, d_2 initiation reaction parameters
 d desired value
 f final (reactor exit)
 j_i i^{th} jacket ($i=1:5$)
 o oxidation
 p propagation
 trs chain transfer to solvent
 z_j j^{th} location along the reactor length

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