CHEMICAL ENGINEERING TRANSACTIONS

VOL. 56, 2017

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim
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ISBN 978-88-95608-47-1; **ISSN** 2283-9216

DOI: 10.3303/CET1756126

Comparison Study of Model Based Industrial Low-Density Polyethylene Production in Tubular Reactor

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The challenges of Low-Density Polyethylene (LDPE) industry kept growing, and manufacturers have to come out with solutions to debottleneck the reactor output while abiding to the stringent product specification. One of the way to cope with this is through computational modelling. In the present study, the process behaviour approximation of LDPE production in tubular reactor (TR) was represented by computational model. Three models were compared and critically discussed in this paper. Plots of reactor temperature along the axial length of TR for all the models were shown and significant variations were observed between each model. The results depict that higher rate constant for propagation give higher temperature profile, and different rate constant for initiator decomposition produce dissimilar rate of polymerisation. In the later section, a comparison study of varying the amount of initiator at reactor inlet versus adding extra injector to a LDPE tubular reactor (LDPE-TR) was conducted and the results were showed in the form of temperature and monomer conversion profile.

1. Introduction

Polyethylene, which includes HDPE, LDPE and LLDPE are the most common polymer worldwide. The total production of polyethylene is estimated around 80 Mt/y, and LDPE alone contribute 30 % of the total volume of produced polyethylene. The global LDPE production reached over 35 Mt in 1994, and has been reported to growth rapidly at the proportion of 7 %/y over the past 15 y (Yao et al., 2004). A highly flexible and branched LDPE, has density in the range of 0.910 – 0.940 g/cm^3 and can withstand temperatures of 98 °C up to 115 °C. A single polyolefin plant can produce up to forty grades of LDPE with various melt flow index (MFI). The number-average molecular weight for LDPE is 21,900 g/mol as reported by Asteasuain et al. (2001). LDPE is produced in either tubular reactors or stirred autoclave vessels. Before 90's, the majority of LDPE (60 %) was produced in the autoclave reactors but afterwards the tubular reactors were gradually selected to be used. At the present time, the TR stands for 60 % of the total production of LDPE. This present study deals on the production of LDPE in TR (Erdeghem et al., 2010).
A typical high-pressure LDPE-TR is made of a very long spiral-wrapped jacketed metallic pipe with the accumulated length of the tube ranging from 500 to 3,300 m. The TR is configured as a series of straight sections joined by 180 degree bends. The inner diameter is in the ranges of 60 - 80 mm (Yao et al., 2004) whereas the outer diameter ranging from 160 to 180 mm. Thick wall layer is employed to the reactor tube in order to handle the extreme operating condition involved in the polymerisation of ethylene. The current industrial high pressure TR is utilised on ratios of length to diameter (L/D) ranging from 1 – 6 × 10^{-4} (Yao et al., 2004). The TR has several reactions, heating and cooling zones. In the pre-heating and cooling zones, the control of the reaction mixture temperature is achieved by circulating steam or liquid water through different jacket zones. Figure 1 shows the schematic diagram of the high-pressure LDPE-TR production line. Ethylene, along with initiators and chain transfer agents (CTA), are used to produce low-density polyethylene (LDPE) via free radical polymerisation in a TR at extreme conditions, typically at pressures of 1,500 – 3,000 atm and temperatures of 50 – 350 °C. Ethylene polymerisation is a highly exothermic reaction, immediately after the introduction of peroxides, a sharp increase of temperature and conversion will occur in a short reaction zones signalling to the ethylene polymerisation process. The subsequent sections of the TR are mainly utilised as

Please cite this article as: Azmi A., Aziz N., 2017, Comparison study of model based industrial low-density polyethylene production in tubular reactor, Chemical Engineering Transactions, 56, 751-756 DOI:10.3303/CET1756126

heat exchangers in order to reach appropriate temperatures for peroxide addition or for downstream process. The conversion of ethylene in this reactor is reported to be 20 - 35 % per pass (Agrawal et al., 2006).

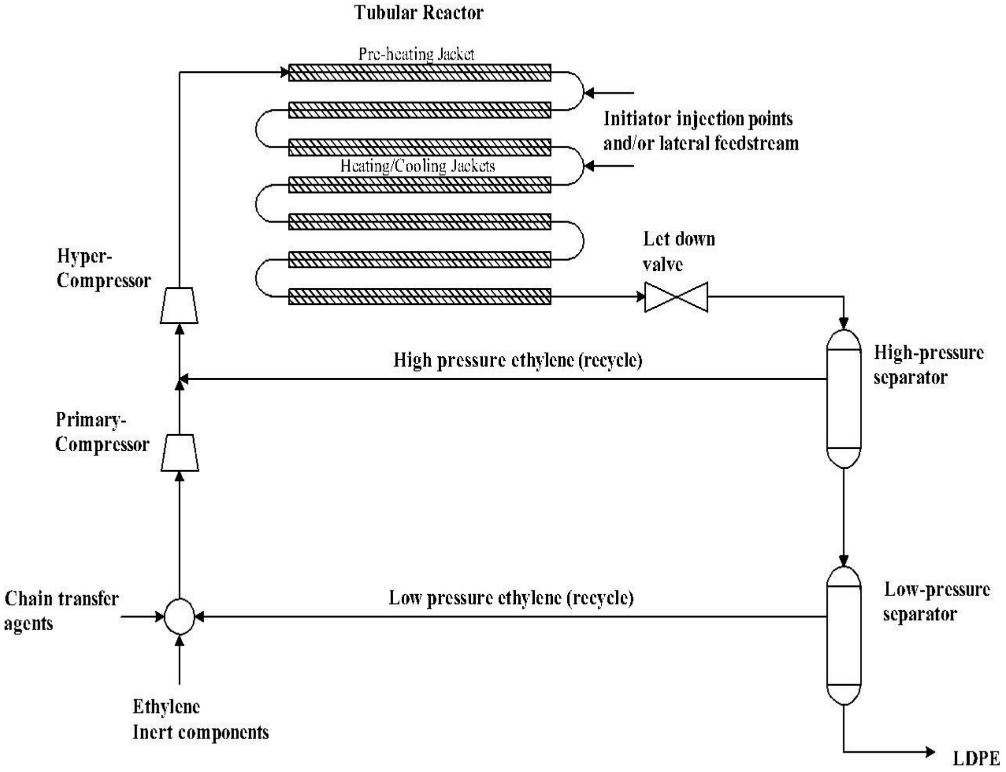

Figure 1: Simplified flow diagram of LDPE plant

A mathematical model is a fundamental tool for researchers and engineers in this field. It allows safe and economic study of the intricate connection between design variation and operative variables on output, which are mainly related to production and product quality. Despite being a complex task, numerous studies have been conducted to model and simulate the LDPE-TR. Asteasuain et al. (2001) used steady-state assumption for parameter adjustment through a reduced mathematical model. Erdeghem et al. (2010) works emphasising on boosting the LDPE productivity while reducing the investment cost. They used pareto-optimal study of multi-peak models to identify where along the TR and how much the amount of initiator has to be injected to increase the profit margin. Zavala and Biegler (2009) derive a general nonlinear model predictive control (NMPC) to optimise the operation of LDPE-TR by stabilising the TR in the case of persistent fouling disturbances.

The most recent studies on LDPE modelling and simulation reported in the literature justify the importance and relevancy of computational model in LDPE production. Fries et al. (2016) carried out study on fouling in TR through experiment and computational approach. Copelli et al. (2016) investigate the runaway problems in unsteady state TR. Pladis et al. (2015) proposed a predictive computational model to describe the viscoelastic behaviour of LDPE produced in high pressure TR. While researches on modelling and optimisation are abundant in the literature, comparison study between the developed models can be rarely found. In this paper, three mathematical models namely Azmi and Aziz (2016), Gupta et al. (1985) and Yao et al. (2004) with the most comparable set of equations and operating conditions were compared and critically discussed. All this models were chosen due to their proximity to each other in terms of equations and operating conditions applied. In the later part, a comparison study of varying the amount of initiator at reactor inlet versus adding extra injector to a LDPE TR was conducted.

2. Model and Simulation

All three mathematical models used for comparison study were modelled based on the same assumptions which are:

1. Ideal plug flow condition (i.e., there are no radial temperature gradients in the TR, and no axial mixing). These assumptions are valid for this study due to high Reynolds number (Agrawal et al., 2006) and very high L/D ratio. (Where L is the total length reactor and D is the inside diameter of TR)
2. The pressure inside reactor is constant throughout the reactor since the pressure drop is less than about 10 % of the mean value, which are not significant (Gupta et al., 1985).
3. Pulse valve effect is not included in the model as inferred from pilot plant studies by Donati et al. (1982).
4. Homogenous phase (single phase) of ethylene and polyethylene is assumed as suggested by Ehrlich and Mortimer (1970).
5. The heat capacity of reaction mixture is represented as total heat capacities of pure components (Yao et al., 2004).

In the next comparison study of varying the amount of initiator at reactor inlet versus adding extra injector, the model equations and parameters, kinetic mechanisms and rate constants were given in Table 1 and Table 2. Eqs(1) – (4) constitute the mass balance on each component in the reactor, whereas Eq(5) represents the heat transfer from the reaction mixture to the jacket coolants. The density variation was present in Eq(6) – (8) followed by the physical properties of the reaction mixture and TR which are described in the Eq(9) – (22). MATLAB R2015a® is used to solve all the ODEs. With regards to computational aspects, the axial length (z) of plug flow reactor (PFR) model is divided into two intervals (reaction and cooling zones) to provide stability, thus allowing an effective computational execution. The differential equations are solved using ode23 solver.

3. Results and Discussion

The mathematical model plots are presented in Figure 2. As mentioned before, all this models were chosen due to their proximity to each other in terms of equations and operating conditions applied. The most notable differences are the reactor inlet temperature, kinetic scheme and sets of reaction constants. From previous studies, inlet temperature give significant effect on the monomer conversion and insignificant effect to the temperature. It was reported that 10 °C different in reactor feed temperature parameters may not cause reaction temperature peaks to differ more than 10 °C (Gupta et al., 1985). From Figure 2, it was noticeable that the differences in temperature peaks between Gupta et al. (1985) to Yao et al. (2004) and Azmi and Aziz (2016) are very high, which was more than 40 °C. It is believed that there exists other major influence to this significant variation, notably the different in rate constants applied.

The fact that reaction rate constant play significant role to the reactor temperature peak was highlighted by numerous researchers. Brandolin et al. (1988) clearly stated that kinetic rate constants for peroxide initiation, propagation and termination are determinant of temperature and ethylene conversion profile, whereas rate constants of thermal degradation, transfer to solvent and transfer to polymer are determinant of Number Average Molecular Weight (Mn), Weight Average Molecular Weight (Mw) and Polydispersity Index (PDI) The rate constants of propagation and initiation for all three models were differs to one another. Propagation rate constant applied in Gupta et al. (1985) model is the highest if compared to the other models. From this information, it is reasonable to mention that higher rate constant of propagation will produce higher temperature peak. Yao et al. (2004) utilised on the same propagation rate constant. However, temperature peak in Azmi and Aziz (2016) model is higher than Yao et al. (2004). This is true since, both models have applied different rate constant of initiation in their mathematical model even though they used similar propagation rate constant. It is believed that different in initiation rate constant will generate dissimilar rate of ethylene polymerisation. Two temperature peaks were observed in Yao et al. (2004) model since they had added second injector to their model.

Figures 3 and 4 compare between increasing the amount of initiator at reactor inlet versus adding extra injector to a LDPE tubular reactor (LDPE-TR). Two temperature peaks were observed in multiple injector's TR due to the occurrence of second propagation reaction as shown in Figure 3. The total amount of initiator injected in the multiple injectors TR is the same amount as the initiator injected at the inlet of single injector TR. It was observable that monomer conversion (XM) for multiple injector TR was higher compared to single injector TR as shown in Figure 4. The highest XM of single injector TR is 23.20 %, observed at axial length of 120.30 m while the accumulative XM of multiple injector TR was 27.83 % observed at axial length of 637.25 m. It seems that there exists a considerable amount of initiator in the single injector TR that might not decompose or in other words might not turn into radicals, thus reducing the efficiency of monomer conversion. Figure 5 demonstrates how the initiator is fully utilised during the polymerisation reaction. Even though both reactor had consumed the same amount of initiator (1.5 x 10^{-3} mol/L), however with the inclusion of second injector (in the multiple injector TR) the efficiency of monomer conversion get improved. It was assured that efficiency of monomer conversion will increase if additional initiators are introduced in the later stage inside TR.

Table 1: Model Equations for the LDPE-TR

Descriptions	Equation	
Overall mass balance	$\frac{dv}{dz} = -\frac{v}{\rho}\left(\frac{d\rho}{dz}\right)$	(1)
Initiator balance	$v\frac{dC_{I_m}}{dz} = \left(-2fK_{d_m}C_{I_m} - C_{I_m}\frac{dv}{dz}\right) \quad \therefore \text{for } m = 1, 2$	(2)
Monomer balance	$v\frac{dC_M}{dz} = \left(2K_{th}{C_M}^3 - K_{trm}C_M\lambda_0 - C_M\frac{dv}{dz}\right)$	(3)
Solvent balance	$v\frac{dC_S}{dz} = \left(-K_{trs}C_S\lambda_0 - C_S\frac{dv}{dz}\right)$	(4)
Reactor temperature	$\frac{dT}{dz} = \frac{1}{\rho C_P v}\left[-\Delta H K_p C_M \lambda_0 - \frac{4U(T - T_J)}{D}\right]$	(5)
Reaction mixture density variation	$\frac{d\rho}{dz} = \frac{\partial\rho}{\partial T}\frac{dT}{dz} + \frac{\partial\rho}{\partial C_M}\frac{\partial C_M}{dz}$	(6)
where		
	$\frac{\partial\rho}{\partial T} = \frac{1.436 \times 10^{-6}C_M - 2.5245 \times 10^{-4} + (31.6967 - 1.25C_M) \times 10^{-8}\,T - 9.98877 \times 10^{-11}\,T^2}{(0.71 - 4.475 \times 10^{-4}\,T)^2(0.949 + 4.988 \times 10^{-4}\,T)^2}$	(7)
and	$\frac{\partial\rho}{\partial C_M} = 0.028\left(\frac{1 - 0.71 - 4.475 \times 10^{-4}\,T}{0.949 + 4.988 \times 10^{-4}\,T}\right)$	(8)
Overall heat transfer coefficient	$U^{-1} = h_i^{-1} + h_w^{-1}$	(9)
Reaction mixture density (g/cm^3)	$\rho = \frac{1 + 0.028C_M(V_P - V_M)}{V_P}$	(10)
Specific heat of reactant mixture (cal/g.K)	$C_p = 0.518w_m + (1.041 + 8.3 \times 10^{-4})w_p$	(11)
Heat of reaction (cal/mol)	$-\Delta H = 23000$	(12)
Moment of live polymer radical	$\lambda_0 = \sqrt{\frac{2fK_{d_m}C_{I_m} + 2K_{th}{C_M}^3}{K_{tc}}}$	(13)
Reactor side heat transfer coefficient (cal/cm^2.s.K)	$h_i = \frac{K(Nu)}{D_i}$	(14)
Thermal conductivity (cal/cm.s.K)	$K = (5w_m + 3.5w_p) \times 10^{-4}$	(15)
Nusselt Number	$Nu = 0.026Re^{0.8}Pr^{0.33}$	(16)
Reynolds Number	$Re = \frac{\rho D_i v}{A_c \eta_s}$	(17)
Viscosity of reactant mixture (Poise)	$\eta_s = \eta_r \eta_o$	(18)
Relative viscosity of monomer	$\eta_r = 10^{0.0313\sqrt{\mu_{00}^{-1}\mu_{00}^{3}}}$	(19)
Viscosity of monomer, Poise	$\eta_o = 1.98 \times 10^{-4} + 1.15 \times 10^2\,T^{-2}$	(20)
Prandtl Number	$Pr = \eta_S C_P / K$	(21)
Heat transfer coefficient for metal wall (cal/cm^2.s.K)	$h_w = 0.025$	(22)

Table 2: Rate constants and parameters used in this study (Azmi and Aziz, 2016)

Rate of reaction constant (1/s)	
Rate constant of monomer thermal initiation, K_{th}	$6.04 \text{ x } 10^{3} \exp[-36{,}707(T+273.15)^{-1}]$
Rate constant of propagation, K_p	$9.90 \text{ x } 10^{5} \exp[-1{,}982(T+273.15)^{-1}]$
Rate constant of termination by combination, K_{tc}	$4.40 \text{ x } 10^{4} \exp[-377.2(T+273.15)^{-1}]$
Rate constant of chain transfer to monomer, K_{trm}	$1.20 \text{ x } 10^{5} \exp[-6{,}758(T+273.15)^{-1}]$
Rate constant of chain transfer to polymer, K_{trp}	$1.80 \text{ x } 10^{8} \exp[-4{,}730.3(T+273.15)^{-1}]$
Rate constant of β-scission to secondary radical, K_{β}	$1.40 \text{ x } 10^{9} \exp[-9{,}371(T+273.15)^{-1}]$
Rate constant of β-scission to tertiary radical, $K_{\beta 1}$	$4.40 \text{ x } 10^{9} \exp[-9{,}371(T+273.15)^{-1}]$
Rate constant of chain transfer to solvent, K_{trs}	$5.60 \text{ x } 10^{7} \exp[-5{,}290(T+273.15)^{-1}]$
Rate constant of peroxide initiation, K_d	$6.50 \text{ x } 10^{11} \exp[-12{,}800(T+273.15)^{-1}]$
Parameters	
Tubular reactor length, L (m)	1,200
Reactor diameter, D (m)	0.05
Pressure, P (atm)	2,000
Initial concentration of monomer, C_{M0} (mol/L)	19.54
Initial concentration of initiator, C_{I0} (mol/:)	$1.5 \text{ x } 10^{-3}$
Initial reaction mixture velocity, v_o (m/s)	18.8
Feed Temperature, T_F (°C)	140
Jacket Temperature, T_J (°C)	180

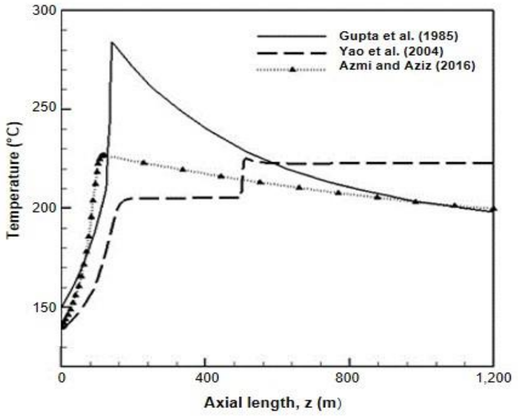

Figure 2: Reactor temperature profile with regards to its axial distance from previous studies

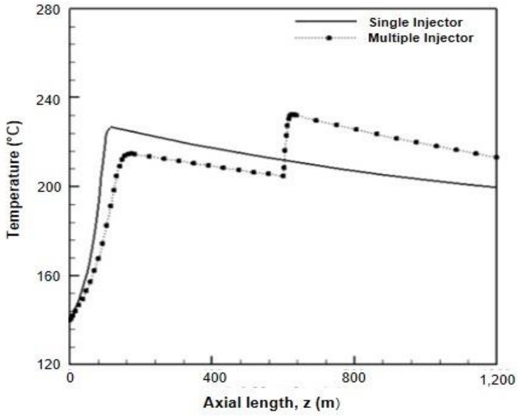

Figure 3: Reactor temperature profile with regards to its axial distance

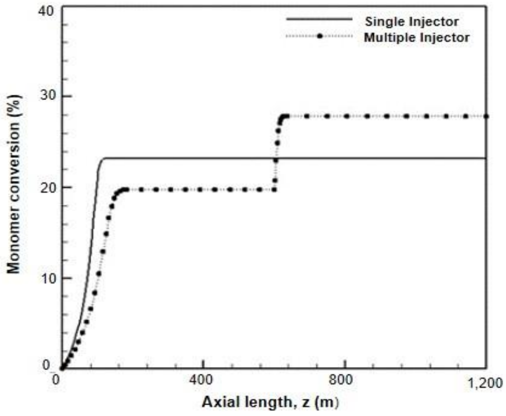

Figure 4: Axial variation of monomer conversion

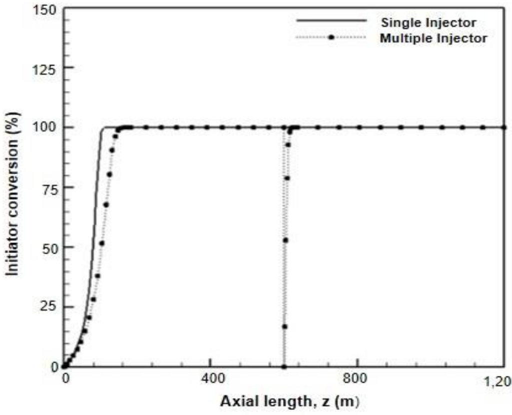

Figure 5: Axial variation of initiator conversion

The declining reaction temperature in the multiple injector curve (Figure 3) was due to the cooling process. Reaction mixtures were immediately cooled to the optimal temperature level for the half-life of the second initiator injection. It was identified that initiator is highly temperature dependent and requires optimum temperature in the range of 160 – 180 °C for the decomposition process. In worst case scenario, if temperature level goes beyond this range, the radicals will be spoiled and no way will free-radical polymerisation occur. In the cooling section of both single and multiple injector, no reaction was taking place and therefore absolute zero monomer conversion was observed in this section. In industrial practice, whole temperature profiles are controlled by manipulation of feed inlet, jacket heating/cooling inlet and initiator flow rates.

4. Conclusion

The present study strengthens the fact that reaction rate constants play significant role to the reactor temperature peak. In this research context, it was revealed that higher propagation rate constant produce higher temperature peak and different initiation rate constant generate dissimilar rate of ethylene polymerisation. In the comparison study between increasing the amount of initiator at reactor inlet versus adding extra injector to a LDPE-TR, it is proven that spreading the initiator (additional injector) along the TR will help improving the efficiency of initiator decomposition thus increasing the ethylene conversion. In the future, it will be very beneficial to conduct a cost effectiveness study of adding extra injector versus increasing the amount of initiator at reactor inlet. Inclusion of actual plant data to the current model plot will also be advantageous for comparison study.

Acknowledgement

The financial support from Universiti Sains Malaysia through Research University Grant No. 1001/PJKIMIA/814237 and MyBrain15's Fund from Ministry of Higher Education Malaysia to the first author are greatly acknowledged.

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