Simulation and Sensitivity Study of Industrial Low Density Polyethylene Tubular Reactor

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The development and application of process modelling technology for polymer industry is relatively increasing. Accurate simulation of the polymerisation process can help industrial community to maximise their polymer production with minimal energy and cost. In this study, industrial Low Density Polyethylene (LDPE) tubular reactor process has been simulated using Aspen Plus software. Aspen Polymer (Aspen Plus component) was used to model the free radical polymerisation part of the polymer. The reactor properties, reaction mechanisms and kinetic model for the polymerisation process was taken from several referred journals. Sanchez-Lacombe equation of state was used to describe the thermodynamic properties of the process. Based on a comparison with available literature data, the selected equation of state and reaction kinetic model had performed well in simulating tubular reactor temperature profile, polymer molecular weight and monomer conversion. Sensitivity study was also conducted to study the behaviour of controlled parameters in the tubular reactor process. In this study, the effect of initiators flow rate, oxygen flow rate, and Chain Transfer Agent (CTA) flow rate towards ethylene conversion and temperature profile were observed. From the sensitivity study, both initiators and oxygen flow rate had displayed considerable effect on the observed parameters. Among them, the second initiator flow rate displayed the most significant effect. CTA flow rate gave the minimal effect since its main purpose is to modify the polymer molecular properties. This demonstrates the important of proper regulation of second initiator flow rate in order to meet desired polymer conversion while maintaining the reactor temperature.

1. Introduction

Advancement in various polymer process modelling technologies have made it possible to develop high fidelity polymer process models that can be used for process design and process optimisation (Vale et al., 2013). As a result, the polymer process modelling technology has been well accepted by polymer manufacturing industries. One of the polymer that received wide attention in polymer manufacturing industry is low density polyethylene (LDPE). LDPE is known as a versatile commodity polymer with various application including packaging, adhesives, coatings and films (Pladis et al., 2015). Simulation and modelling of LDPE has been done many researchers in both steady state and dynamic conditions (Vallerio et al., 2013). Most of the models available have been developed based on mathematical model (PDEs and ODEs), which requires a lot of efforts to develop, high complexity and tailored to a specific type of polymer only. The development of computer-aided design (CAD) tools in polymer modelling has grown from before to overcome these problems. Most of them have modular system, user friendly interface, model based design approach and support numerous polymer type and reaction. Asteasuain et al. (2001) used gPROMS® (Process System Enterprise) to simulate dynamic simulation of LDPE tubular reactor. Based on the model, they had proposed an optimal reactor start-up strategy which can maximise the polymer conversion and production rates while keeping a safe reactor operation. Bokis et al. (2002) presented a comprehensive methodology for developing a steady state model of LDPE tubular reactor process using Polymer Plus® (Aspen Tech). In their work, perturbed-chain statistical associating fluid theory (PC-SAFT) was used as the tubular reactor model's equation of state. Both simulation models from the authors have been successfully validated using industrial data. The objective of this study is to simulate steady state industrial LDPE tubular reactor using Sanchez-Lacombe (SL) equation

of state and conduct sensitivity study of the process. SL equation of state is selected based on its ability to model thermodynamic properties of polymeric process (Guerrieri et al., 2012). SL equation of state had been applied by many researchers previously to model liquid-liquid equilibrium for example in flash separator (Pladis et al., 2014). The information on the LDPE tubular reactor model and kinetic parameters are mainly obtained from Asteasuain et al. (2001) and Agrawal et al. (2006). In this study, Aspen Polymer® (previously known as Polymer Plus) is used to simulate the polymerisation process (Aspen Polymer, 2016). In term of sensitivity study, several manipulated parameters are selected to observe its effect towards polymer conversion (which related to plant profits) and reactor temperature (which related to plant safety). The selected parameters are initiators flow rate, oxygen flow rate, and Chain Transfer Agent (CTA) flow rate. The output of the study will help to identify the most appropriate parameter to be used to control the polymer conversion and reactor temperature.

2. Methodology

2.1 Equation of state

Guerrieri et al. (2012) had conducted a good review on application of equation of state (EOS) in polymer modelling. They concluded that development of EOS for polymers still remains an active area of research and it is difficult to recommend a specific EOS for certain application. Among popular EOS in polymeric system are Sanchez-Lacombe (SL), Statistical Associating Fluid Theory (SAFT) and Perturbed-Chain SAFT (PC-SAFT). In this study, SL EOS was selected to model LDPE thermodynamic properties and phase behaviour. SL EOS is one of the simplest statistical mechanics thermodynamic models that are capable of describing the phase behaviour of a multi component (monomer-polyolefin) system (Pladis et al., 2014). SL EOS parameters used in this study were taken from Aspen Technology (2012) and Orbey et al. (1998).

2.2 Heat of Polymerisation

Heat of polymerisation is the difference between enthalpy of produced polymer and enthalpy of monomer. The ideal-gas enthalpy of ethylene is available in Aspen Plus database. The ideal-gas enthalpy of LDPE polymer is estimated using equation of state since this is a property that cannot be measured experimentally. In Aspen Polymer, since LDPE is a homopolymer system, the polymer enthalpy is equal to the enthalpy of the monomer segment. The heat of formation (DHFVK) of the ethylene segment is fine-tuned until the reported heat of polymerisation matched with literature (Bokis et al., 2002). The calculated heat of formation for ethylene and ethylene (segment unit) was reported to be -2.15×10^7 J/kmol and -3.357×10^7 J/kmol (Bokis et al. 2002). Heat of polymerisation plays a significant role in shaping the reactor temperature profile and attaining the desired polymer conversion.

2.3 Reactor Modeling and Simulation

In this simulation, RPLUG model in Aspen Plus was used to simulate the tubular reactor. Ideal plug flow conditions can be assumed for the reactor model based on its high Reynolds (Re) numbers and high L/D (reactor length over reactor diameter) ratio (Zabisky et al., 1992). The flow of the mixture inside the reactor is assumed to be homogeneous (single phase). In the polymerisation process, gaseous (supercritical) ethylene monomer is converted into amorphous liquid LDPE. The reactor model was divided into five smaller parts to represent the reactor zones. The reactor jacket temperature was set to remains constant at each zone and equal to the average between the inlet and output jacket temperature of the corresponding zone. Asteasuain et al. (2001) demonstrated that considering the jacket temperature constant by zones would allow a good prediction of temperature profiles for the reacting mixture during steady state condition. Constant thermal fluid temperature and heat transfer coefficient was used for each zone in the reactor model. The reactor feed contains ethylene monomer, *n*-butane as inert solvent, oxygen and propane as chain transfer agent (CTA). Oxygen was used to produce initiator radical to assist polymerisation process and improve conversion. Inert solvent was used to control the molecular weight of polyethylene by the process of chain transfer to the solvent (Agrawal et al., 2006). The addition of CTA in the mixture can avoid the production of prohibitively large polymer molecules which would increase viscosity interfering with heat transfer and with the thermal control of the reactor (Asteasuain et al., 2001). The pressure drop along the reactor is estimated to be approximately 10 % from the reactor inlet pressure as observed in industrial practice (Bokis et al., 2002). The reactor design parameters and feed conditions are available from Asteasuain et al. (2001) and Agrawal et al. (2006).

2.4 Kinetic Mechanism

High pressure free radical ethylene polymerisation is used in many industrial LDPE productions. Study on the kinetic mechanism and its rate constant has been done extensively by many authors and in many versions.

The latest is a review done by (Azmi and Aziz, 2016). The authors had compared kinetic mechanisms from several sources and also reviewed some of the rate constants for available in the literature. They noted that there were some discrepancies from the authors regarding LDPE kinetic mechanisms and rate constants. Selection of these parameters should be based on case by case scenario. The kinetic mechanisms were selected by reviewing work from Agrawal et al. (2006). The kinetic mechanisms used were initiator decomposition, oxygen decomposition, chain initiation, chain propagation, termination by combination, chain transfer to monomer, chain transfer to polymer, chain transfer to transfer agent, chain transfer to solvent, β-scission and short chain branching. It should be noted that termination by disproportion mechanism was excluded since it was not used by many authors (Brandolin et al., 1996). The rate constant used in this LDPE polymerisation is listed in Table 1. Most of the kinetic rate constants were selected based on Agrawal et al. (2006) study. The initiator kinetic rate constants used are within acceptable range (Brandolin et al., 1996) and kinetic rate constants for chain initiaition and propagtion are assumed to be the same (Bokis et al., 2002). The initiator decomposition kinetic rate constant for oxygen is taken from Brandolin et al. (1996) work. The initiator efficiency represents the fraction of generated radicals that are effective in initiating polymer chain growth. Initiator efficiency is adjusted to match the validation temperature profile.

Table 1: Kinetic rate constants used in Aspen simulation

Reaction Type (Aspen Polymer)	k_o 1/sec	E_a J/kmol	V* m^3/kmol	Efficiency
Init-Dec (Initiator 1)	1.00×10^{14}	1.320×10^8	0.0140	0.90
Init-Dec (Initiator 2)	1.00×10^{12}	1.265×10^8	0.0116	0.90
Init-Dec (O_2)	1.60×10^{11}	1.359×10^8	-0.0121	0.16
Chain-Ini	4.00×10^5	1.740×10^7	-0.0168	
Propagation	4.00×10^5	1.740×10^7	-0.0168	
Chat-Monomer	1.01×10^8	7.939×10^7	-0.0051	
Chat-Polymer	5.20×10^4	3.680×10^7	-0.0190	
Chat-Agent	7.00×10^4	1.841×10^7	0.0000	
Chat-Solvent	7.00×10^4	1.841×10^7	0.0000	
B-Scission	1.40×10^9	8.475×10^7	-0.0099	
Term-Comb	8.70×10^8	1.528×10^7	0.0092	
Sc-Branch	1.20×10^{10}	6.054×10^7	0.0000	

3. Results and Discussion

3.1 Model results and validation

The result for Aspen model validation is shown in Figure 1. Based on the figure, Aspen model has managed to simulate most of the industrial tubular reactor temperature data. The slight discrepancy is noticeable at reactor length 850 m to 1,000 m occurred in zone 5. At this length, second initiator is introduced to the process to resume the polymerisation reaction. It appears that second initiator used by the industry has higher temperature release than Aspen model during the radical initiation period. The reason for this dissimilarity is possibly due to different selection in second initiator kinetic parameters. A tight control of reactor temperature profile could ensure similar molecular weight, molecular weight distribution and density of polymer throughout the process (Butler, 2010). Aspen model temperature profile is similar with temperature profiles found in actual industrial reactors which show a rounded peak and followed by a slow temperature decrease (Bokis et al., 2002). Table 2 verifies the molecular properties of the simulated LDPE polymer against industrial data. Based on the table, all properties are in good agreement with industrial data. The LDPE density is controlled by the Short-chain (SCB) and Long Chain (LCB) branch concentration inside the polymer.

Table 2: Comparison of selected parameters between Aspen Model and industrial data

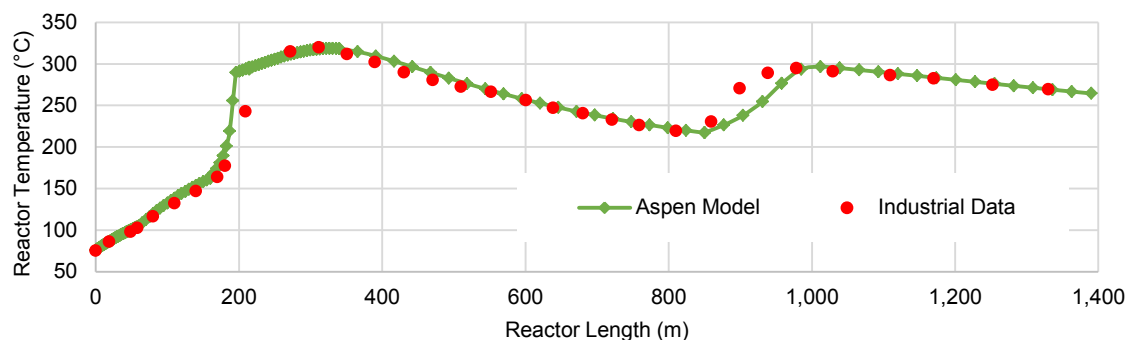| Property	Industrial Data	Aspen Model
Final ethylene conversion	30 %	29 %
Number Average Molecular Weight (MWN)	21,900 g/mol	20,964.22 g/mol
Density of polymer mixture	530 kg/m^3	531.3851 kg/m^3 (exit from Zone 5)

Figure 1: Aspen model temperature profile validation with industrial data from Asteasuain et al. (2001)

3.2 Sensitivity Study

The sensitivity study was performed using Model Analysis Tool in Aspen Plus. The results are shown in Figure 2 to Figure 5. Figure 2 shows the effect of first initiator flow rate variation towards ethylene final conversion and zone 5 maximum temperature. Based on the figure, the highest conversion can be achieved by the first initiator is at 1.15 kg/h with ethylene conversion 29.8 % and temperature 289.5 °C. After the optimum peak, adding more initiator will only decrease ethylene conversion and zone temperature. This phenomenon is further study in Figure 3. This figure presents the effect of first initiator towards ethylene conversion and max temperature in zone 3. In the figure, the first initiator behaves normally in increasing the conversion and temperature of the process as the flow rate increased. It is preferred to study the initiator profile in the zone of which it had injected. The effect of the second initiator can be observed in Figure 4. Based on the figure, second initiator flow rate is directly proportional with ethylene conversion and maximum temperature in Zone 5. In order to achieve ethylene conversion 30 % and above, the second initiator should be increased from 0.576 kg/h to at least 1.16 kg/h with maximum temperature Zone 5 at 311 °C. Similar trends on initiator behaviour can be referred to Dhib and Al-Nidawy (2002) work. The effect of oxygen flow rate in the process is shown in Figure 5. Based on the figure, adding more oxygen can increase the ethylene conversion. However, the maximum temperature in zone 5 had increased drastically and reached 340 °C before the ethylene conversion could achieved 30 %. Based on Brandolin et al. (1996) study, free radicals from oxygen can influence the reactor temperature profile shape and conversion. In practice, the reactor temperature is maintained between 150 °C to 330 °C. There is a possibility of ethylene decomposition during temperature above 340 °C, which can cause thermal runaway inside the reactor (Butler, 2010). Further discussion on thermal runaway is available from Copelli et al. (2016) study. Temperature in Zone 5 had a low interference with the oxygen flow rate variation in the process. It probably due to the fact that oxygen had mostly decompose into free radicals before entering Zone 5. The effect of CTA is not presented since the result shows that the parameter has minimal influence towards the parameters studied. The purpose of CTA is more towards to control molecular property of the polymer such as molecular weight and branching (Kiparissides et al., 2005). Based on the results, initiator flow rate shows the potential to be used to control polymer conversion and maintaining the reactor temperature (Zavala and Biegler, 2009).
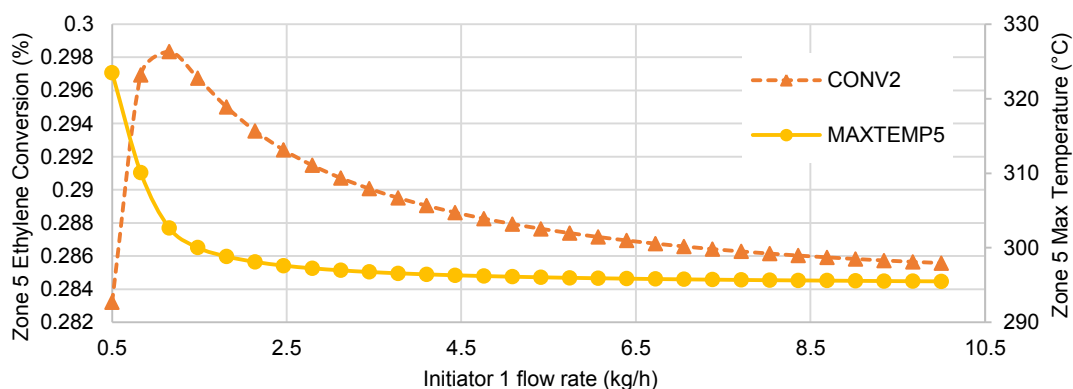

Figure 2: Effect of first initiator flow rate towards ethylene conversion and Zone 5 maximum temperature
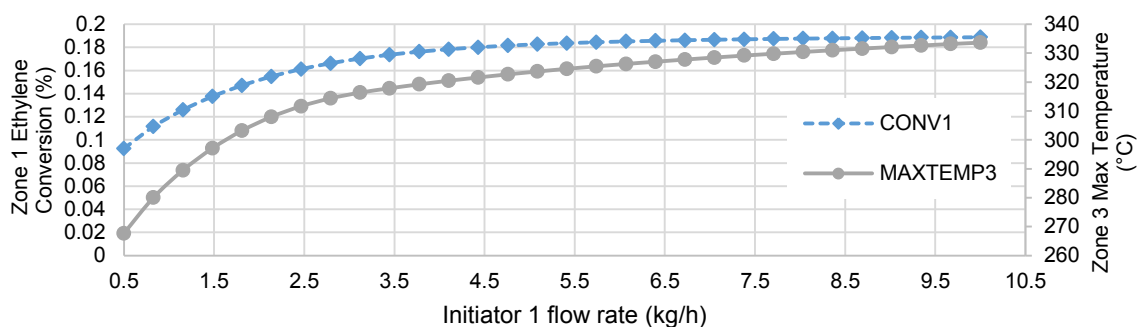
Figure 3: Effect of first initiator flow rate towards ethylene conversion and Zone 3 maximum temperature
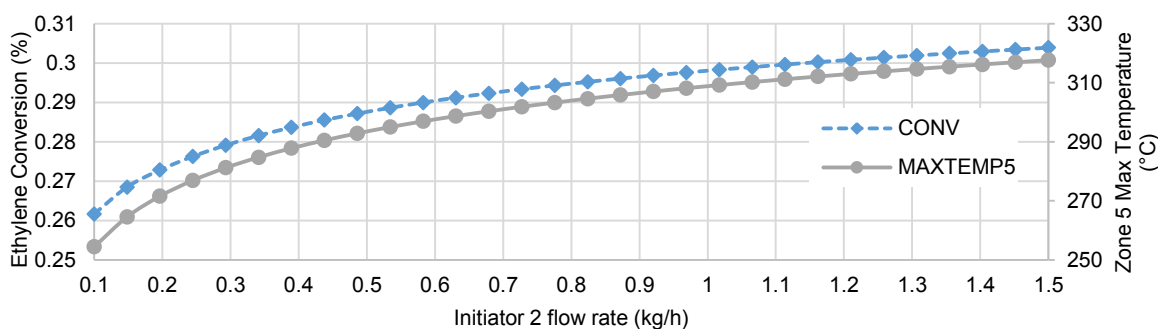

Figure 4: Effect of second initiator flow rate towards ethylene conversion and Zone 5 maximum temperature
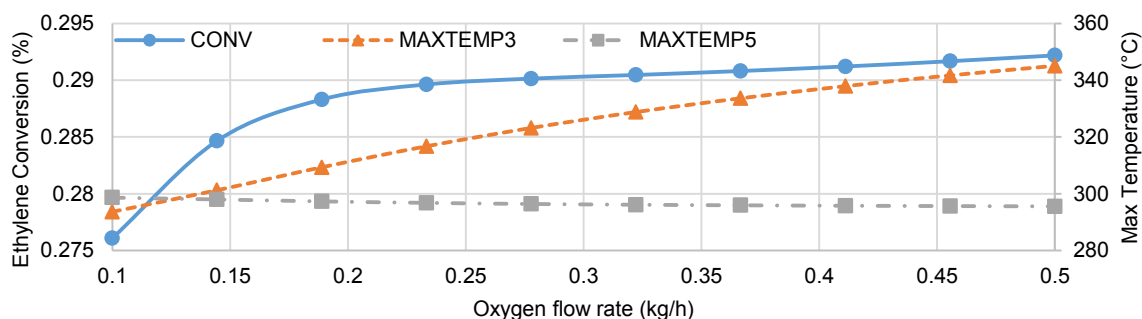

Figure 5: Effect of oxygen flow rate towards ethylene conversion, Zone 3 and Zone 5 maximum temperature

4. Conclusion

In this study, a steady state simulation of industrial LDPE tubular reactor was developed using Aspen Plus software. Sanchez-Lacombe equation of state (SL EOS) was used to simulate the process thermodynamic properties and phase behaviours. The selection of kinetic mechanisms and constants were taken mostly from previous study. The simulation model was successfully validated based on industrial data in term of reactor temperature profile, ethylene conversion, product molecular weight and mixture density. This demonstrate the ability of SL EOS to model the polymer process behaviour properly. In the sensitivity study, initiators flow rate, oxygen flow rate, and Chain Transfer Agent (CTA) flow rate were evaluated based on polymer conversion and maximum reactor temperature. Based on the results, both initiators and oxygen flow rates had exhibited certain effect on the output parameters. CTA flow rate has minimal effects on the output parameters since its original purpose was to modify the molecular properties of the polymer. The molecular properties of the polymer will determine the final polymer physical property for example melt flow index (MFI). Although oxygen has a strong impact on the conversion, its presence in large quantity can lead to thermal runaway inside the reactor which is unsafe for the operation. Both initiators flow rate has displayed direct relationship effects on

the polymer conversion with reasonable temperature ranges. In order to achieve the desired conversion in the production line and maintaining reactor temperature, manipulating the initiators flow rate especially the second initiator flow rate is the best method for such process. This result corresponds to the common industrial practice in controlling tubular reactor. Application of dynamic model offer advantages in term of simulating the process behaviour in real time which is important in safety, control and optimisation area. Future work should focus on the development of dynamic model for LDPE process.

Acknowledgments

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