International Journal of Chemical Engineering and Analytical Science
Vol. 1, No. 1, 2016, pp. 10-17
http://www.aiscience.org/journal/ijceas

Mathematical Modelling and Simulation of an Industrial Propylene Polymerization Batch Reactor

Areej Abbas Abubaker, Mustafa Abbas Mustafa*

Chemical Engineering Department, Faculty of Engineering, University of Khartoum, Khartoum, Sudan

Abstract

The aim of this research is to develop a mathematical model for the propylene polymerization batch reactor for a local petrochemical company. The kinetics of polymerization is based on a single type of active sites on Ziegler–Natta catalyst. The model is composed of a number of algebraic and stiff ordinary differential equations which are solved simultaneously using MATLAB script language. The developed model was used to predict the properties of end-product, which include weight and number average molecular weight, polydispersity index (PDI) and melt flow index (MFI). The simulated batch runs were validated against real batch runs for the values of melt flow index. An average absolute error of 10.8 % was achieved.

Keywords

Propylene Polymerization, Batch Reactor, Mathematical Model

Received: May 24, 2016 / Accepted: June 2, 2016 / Published online: June 20, 2016

1. Introduction

Reusch [1] recorded that prior to the beginning of the 1920's chemists were uncertain about molecules having molecular weights exceeding a few thousand. This theory was then challenged by Hermann Staudinger, who was a German chemist who studied natural compounds such as rubber and cellulose. Despite his doubts, Staudinger has suggested that they were made of macromolecules composed of 10,000 or more atoms. He then came up with a formula for polymeric structure of rubber, which was based on a recurring isoprene unit (monomer). The discovery that polymeric macromolecules are the building blocks of many crucial natural materials was then shadowed by the formation of synthetic analogs having a wide range of properties and features. The application of these materials such as adhesives, resistant paint and durable but light weight solids has transformed our modern world.

Fogler [2] defines polymerization as "the process in which monomer units are linked together by chemical reaction to form long chain, which gives polymers their unique characteristic properties". He expected that the production of polymers will reach 200 billion pounds in the coming years due to the replacement of metals with higher-strength plastics and composite materials in automobiles and other products. According to Villa [3] polypropylene is normally made using heterogeneous catalysts in liquid or gas-phase reactors. A typical fourth-generation Ziegler-Natta catalyst for propylene polymerization can easily reach a mileage of 30-80kg polymer/g catalyst.

The behaviour of a polymerization reactor is not different from the behaviour of any other reactor, so the same engineering principles apply in both cases. Most polymerization reactions are strongly exothermic, which demands reactor configurations with adequate rates of heat removal. There are many important variables, which are related to end-use polymer properties, which cannot be measured on-line or can only be measured at low sampling frequencies. The main reason of these difficulties is

---

* Corresponding author
E-mail address: Dr.mustafa.abbas@gmail.com (M. A. Mustafa)

complexity of the physical mechanisms and polymerization kinetics. The main objective of this paper is to validate a modified mathematical model of propylene polymerization, for a batch reactor, based on Shamiri et al. [4] model, against actual batch runs from a local petrochemical company.

2. Literature Review

The polymer industry is definitely not a new one; it has been established since the 19^{th} century. Natural polymers were then chemically treated to produce artificial silk. Synthetic polymers were not worked on until the beginning of the 20^{th} century. Baekeland in 1909 prepared the first synthetic polymeric material using a condensed reaction between formaldehyde and phenol. These polymers currently are used as important thermosetting plastics (phenol formaldehyde resins). Ever since his breakthrough, many polymers have been synthesized and sold for general use. Many of our day to day products derive from polymers, such as plastic, rubber and fibres. The huge polymer market results from extensive work in synthetic organic compounds and catalysts [5].

Understanding the physical properties of a polymer requires knowledge of the length of the polymer chains. Chain length is often expressed in terms of the molecular weight of the polymer chain. However, all synthetic polymers are polydisperse in that they contain polymer chains of unequal length, and so the molecular weight is not a single value but a distribution of chain lengths and molecular weights. The molecular weight of a polymer must therefore be described as some average molecular weight calculated from the molecular weights of all the chains [5]. The number average molecular weight is the statistical average molecular weight of all the polymer chains. The weight average molecular weight takes into account the molecular weight of a chain in determining contributions to the molecular weight average. The more massive the chain, the more the chain contributes to the weight average molecular weight [5].

The first work on modelling a gas-phase polymerization reactor is due to Choi and Ray [6], their objective was to understand the dynamic behaviour of fluidized bed reactors for ethylene and propylene polymerization. Meier et al. [7] studied the temperature profile caused by catalyst segregation in a small scale Fluidized-Bed Reactor (FBR) under semi-batch propylene polymerization. The objective was controlling the particle size segregation in a laboratory scale to attain profiles similar to those found in industrial units. A model capable of predicting temperature profile and molecular weight distribution was developed as a tool to help the problem analysis. The proposed model uses multiple compartment approach, segmenting the reactor in a cone region, the draft tube, and the annulus, all of them considerate as a Continuous Stirred Tank Reactor (CSTR).

McAuley et al. [8] discussed the kinetic simulation of $TiCl_4$coinitiated living carbocationic isobutylene polymerizations governed by dormant-active equilibria, using a mechanistic model. Two kinetic models were constructed from the same underlying mechanism: one using a commercial simulation software package (Predici) which is suitable for the modelling and dynamic simulation of macromolecular processes, and the other using the method of moments.

Kiashemshaki, Mostoufi and Gharebagh [9] used the model by Meier et al. [7] for the polyethylene polymerization with Ziegler-Natta catalyst system. Some correlations were included, which are capable to predict melt index and density of the produced polymer from its mass average molecular weight and simulated results were confronted with actual industrial plant data.

Rosenfeld et al. [10] tested a nitroxide-mediated radical polymerization (NMRP), in a continuous microtube reactor of 900μm inner diameter, of styrene and n-butyl acrylate at high temperature. The impact of the microsystem reactor on the control of the polymerization reaction was investigated and compared to an average labs cale batch reactor. The Prime benefit of this microsystem is its ability to tackle highly exothermic chemical reactions because of its high surface to volume ratio and the possibility to carry out the polymerization process in homogeneous conditions due to its compact characteristic length. The difference between microtube and batch reactors grow as the exothermicity of the monomer grows. In almost all experiments, the microtube reactor gives smallest polydispersity indices. Hence, the use of microstructured reactors can drastically improve the control of the polymerization.

Ibrehema et al. [11] implemented a model for gas-phase catalysed olefin polymerization fluidized bed reactor using Ziegler–Natta catalyst. On this approach four phases were used: bubbles, cloud, emulsion, and solids, each one with its respective mass and heat transfer equations, and reactions occurring at the catalyst surface (solid phase) present inside the emulsion phase. Catalyst type and particle porosity were included in the model, having effect over reaction rates. The temperature and concentration profiles in the bubble and emulsions phases, the effect of catalyst on the system, as well the superficial gas velocity, catalyst injection rate, and catalyst particle growth on the fluidized bed reactor dynamic behaviour were studied, then comparing the results with those of other developed models (i.e., constant bubble size, well-mixed and bubble growth models). Steady state simulation results of molar mass distribution and polydispersity index of the produced polymer were also compared with experimental data.

Mil et al. [12] studied a dynamic model for the emulsion polymerization of styrene within an emulsion batch reactor. The model includes the main steps for styrene polymerization, along with the relevant balance equations. The resulting set of differential equations was solved for the temperature profile and monomer consumption as a function of time. Emphasis was put on the reaction temperature, which is controlled by the jacket temperature. The controller loop, which determines the flow rate of the cooling/heating fluid, is also included. Finally, the advantage of having a rigorous control system in order to have the desired properties in the final product was analysed.

Mjalli and Ibrehem [13] made a statistical study for the relative relationship of each of the effective polymerization process parameters disclosed the best combination of parameters that could be used for optimizing the process model performance. Parameter estimation techniques are then used to find the values of these parameters that reduce an assumed objective purpose. Published real industrial scale data for the process was used as a basis for authenticate the process sample. To extrapolate the model, an artificial neural network approach is used to represent the working relationship of the chosen parameters with the process operating conditions. The developed artificial neural network based correlation was utilized in a fluidized catalytic bed reactor model and prompt under industrial operating conditions. The new hybrid model predictions of the melt flow index and the emulsion temperature were compared to industrial measurements as well as published models. The predictive quality of the hybrid model was superior to other models. The suggested parameter estimation and modelling approach can be used for process analysis and possible control system design and optimization investigations.

A comprehensive and complex mechanistic model describing gas-phase propylene polymerisation was developed by Shamiri et al. [4]. The kinetics of polymerization is based on a multiple active site for Ziegler–Natta catalyst. The model views the polymerization reaction to take place in bubble and emulsion phases. The established model was utilized to predict polymer production rate, number and weigh average molecular weights, polydispersity index, known as PDI, and melt flow index (MFI).

A five staged complex mathematical model was developed by Meng et al. [14]. Its function was to prompt the stable state behaviour of industrial slurry polymerization of ethylene in multiple stage continuously stirred tank reactors. More particularly, the effects of various operating conditions such as inflow rates of catalyst, hydrogen, and co-monomer, on the molecular structure as well as properties of polyethylene as weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index, melt index, density, are completely determined. It is obvious that the proposed comprehensive model is capable of prompting the stable-state operation of an industrial slurry stirred tank reactor series. It is shown that changing the catalyst flow rate, changes constantly the mean residence-time in both reactors, which plays an important role in the establishment of polyethylene architecture properties such as molecular mass and polydispersity. The melt index and density of polyethylene are mainly controlled by hydrogen and co-monomer concentration, respectively.

Lakatos et al. [15] proposed a three scale mathematical model of batch suspension polymerization reactors of vinyl chloride, which is demonstrated and analysed by simulation. The multidimensional population balance equation which is mesp-scale model for monomer-polymer droplets population is fulfilled with the macro-scale heat balance equations for the continuous phase and the cooling agent. This is a hybrid model that involves polymerization reactions in the droplets, random breakage and collective droplets as well as heat and mass exchange between droplets simulated by binary collisions. The model equations are solved by coupled continuous time-Monte Carlo method. The simulation outcomes demonstrated that the temperature increase in droplets results in differences in the polymer properties.

Huang and Xie [16] developed a mathematical model of the molecular weight distribution based on a particle increase model and the kinetic scheme, to simulate the molecular weight distribution of the slurry phase propylene polymerization on a silica-endorsed metallocene catalyst by means of the equations of moments. The model is used to predict molecular weight distribution, including the number-average molecular weight, the weight-average molecular weight, and the polydispersity index. The outcomes indicate that the mass transfer has a high influence on the polymerization reaction, and it can increase the molecular weight distribution especially; moreover, the molecular weight distribution can be evaluated by simulation; the average molecular weight increases as pressure or temperature, and molecular weight distribution shifts to long chain lengths as the effective diffusion coefficient increasing thought the influence is not remarkable; furthermore, the molecular weight distribution's simulation results are calculated, which fit greatly with the experimental data.

Weiss et al. [17] used computational modelling of polymerization reactions to identify inherent factors which result in the widely noticed deviation of chain length distributions in catalyst transfer polycondensation products from the poison distribution expected for ideal living polymerizations. The primary source of these deviations is shown to be related to intermittent deactivation of metathesis pathways which transform the recently added monomer into a chain end capable of further propagation. Maximum departures from ideal behaviour are observed when the rates of processes involved in metathesis are comparable with the rate of polymerization.

Lima et al. [18] applied the fuzzy logic to model discontinuous polymerization reactors. The proposed fuzzy methodology allows the formulation of a global nonlinear long range prediction model from the conjunction of a number of local linear fuzzy dynamic models. The pilot plant scale synthesis of polylactic acid and nylon-6 were chosen for performance assessment of proposed method. Satisfactory results were achieved. Therefore, the proposed technique can be useful to obtain appropriate representations of systems of complex modelling.

Yaghini and Iedema [19] looked into the modelling of the molecular weight distribution of low density polyethylene has been executed for a tubular reactor under realistic nonisothermal conditions and for a series of continuous stirred tank reactors. The model allows for the existence of multiradicals and the occurrence of gelation. The deterministic model is based on a Galerkin finite element approach and puts into place the pseudo distribution concept to target the number of radical sites per chain as the second dimension next to chain length. It was observed that a broad molecular weight distribution (MWD) in a single continuous stirred tank reactor becomes narrower as the number of continuous stirred tank reactors in series increases and is narrowest in the batch reactor.

3. Methodology

3.1. Polymerization Kinetics

The model of propylene polymerization using Ziegler–Natta catalysts containing multiple active sites, which is developed by Shamiri et al. [4] was adopted to describe production rate, molecular weight and its distribution. The index (j) refers to the type of active site. Each site type is associated with different rate constants for formation, initiation, propagation and chain transfer.

Formation of Active Sites

For a typical Ziegler–Natta catalyst potential active sites of type j on the catalyst particle and the co-catalyst react to form active sites:

$$N^*(j) + co - catalyst \xrightarrow{k_f(j)} N(0,j) \qquad (1)$$

Initiation of Active Sites

The active sites react with the monomer to form propagation sites:

$$N(0,j) + M \xrightarrow{k_i(j)} N(1,j) \qquad (2)$$

Propagation

The propagation sites support the growth of living polymer chains. Addition of fresh monomer molecules to active sites increase the length of the chain by one unit as indicated:

$$N(r,j) + M \xrightarrow{k_p(j)} N(r+1,j) \qquad (3)$$

Chain Transfer Reactions

Chain transfer reactions occur with monomers, hydrogen, co-catalyst and spontaneous transfer reactions.

Transfer to Monomer

Chain transfer to monomer reactions can be expressed as:

$$N(r,j) + M \xrightarrow{k_{fm}(j)} N(1,j) + Q(r,j) \qquad (4)$$

Where Q(r, j) is a dead polymer segment of length r which cannot undergo any further reactions. The living polymer chains of length one, N (1, j), can propagate to form new polymer chains.

Transfer to Hydrogen

The main transfer step in industrial propylene polymerization is the transfer to hydrogen. Varying hydrogen concentration in the reactor is the main technique to control molecular weight averages of industrial polypropylene resin.

$$N(r,j) + H_2 \xrightarrow{k_i(j)} N_H(0,j) + Q(r,j) \qquad (5)$$

$$N_H(0,j) + M \xrightarrow{k_h(j)} N(1,j) \qquad (6)$$

These sites become quickly reinitiated by reacting with the co-catalyst. If the co-catalyst is triethyl aluminium, the reinitiation reaction is given by:

$$N_H(0,j) + AlEt_3 \xrightarrow{k_{hr}(j)} N(1,j) \qquad (7)$$

Transfer to Co-Catalyst

For particular reactor operation conditions, especially at elevated polymerization temperatures, transfer to co-catalyst may be considerable. It is, however, generally negligible at normal polymerization temperatures with Ziegler–Natta catalysts.

$$N(r,j) + AlEt_3 \xrightarrow{k_{fr}(j)} N(1,j) + Q(r,j) \qquad (8)$$

Spontaneous Transfer

Spontaneous transfer reactions can be described as:

$$N(r,j) \xrightarrow{k_{fs}(j)} N_H(0,j) + Q(r,j) \qquad (9)$$

This site can undergo initiation reactions with monomer as for transfer to hydrogen.

Deactivation Reactions

Active sites may deactivate spontaneously to generate dead sites and dead polymer chains that are unable to catalyze polymerization:

$$N(r,j) \xrightarrow{k_{ds}(j)} N_d(j) + Q(r,j) \tag{10}$$

$$N(0,j) \xrightarrow{k_{ds}(j)} N_d(j)) \tag{11}$$

$$N_H(0,j) \xrightarrow{k_{ds}(j)} N_d(j) \tag{12}$$

Reactions with Poisons

Existence of catalyst poisons in the polymerization system is considered as one of the worst conditions in industrial polymerization processes. One of the functions of alkyl aluminium catalysts is to passivate the system by removing most of the polar poisons in the reactor prior to catalyst injection and polymerization. Even low levels of some reactive impurities, such as carbon monoxide, can cause a nearly instantaneous drop in propagation rates. Adsorption of such an impurity onto a catalyst site can cause it inactive. These reactions can be shown as follows:

$$N(r,j) + I_m \xrightarrow{k_{dI}(j)} N_{dIH}(0,j) + Q(r,j) \tag{13}$$

$$N_H(0,j) + I_m \xrightarrow{k_{dI}(j)} N_{dIH}(0,j) \tag{14}$$

$$N(0,j) + I_m \xrightarrow{k_{dI}(j)} N_{dIH}(0,j) \tag{15}$$

The reaction rate constants are listed in Table 1.

Table 1. Rate Constants Of The Reactions [4].

Rate Constant	Site Type 1	Site Type 2	Units
$k_f(j)$	1	1	s^{-1}
$k_i(j)$	22.88	54.93	lit/mol.s
$k_h(j)$	0.1	0.1	lit/mol.s
$k_{hr}(j)$	20	20	lit/mol.s
$k_p(j)$	342.8	34.28	lit/mol.s
$k_{fm}(j)$	0.0865	0.2171	lit/mol.s
$k_{fh}(j)$	7.5	7.5	lit/mol.s
$k_{fr}(j)$	0.024	0.12	lit/mol.s
$k_{fs}(j)$	0.0001	0.0001	lit/mol.s
$k_{ds}(j)$	0.00034	0.00034	s^{-1}
$k_{dI}(j)$	2000	2000	lit/mol.s

3.2. Model Development

The model consists of mass balances and moment equations for living and dead polymer, which allow the prediction of the physiochemical characteristics of the polymer such as molecular weight, polydispersity index (PDI) and melt flow index (MFI). The assumptions considered in developing the model are summarized below:

- Mass and heat transfer resistances between the gas and the solid polymer particles are negligible (small catalyst particles, low to moderate catalyst activity or polymerization rates)
- A one-site kinetic scheme.
- No impurities
- The molar flowrate of potential active sites into the reactor is 90% of the molar feed rate of the catalyst.
- The only significant consumption of monomers is by propagation.
- Number of units in polymer chain is not more than two.
- Polymer phase is 60% of volume of reactor.
- Consumption of hydrogen is very small comparing with monomer's consumption.

3.2.1. Mass Balance Equations for Active Sites and Reacted Monomers

Mass balances equations were developed by Shamiri et al. [4], which were modified to meet the model under considerations as followed:

The mass balance on the number of moles of potential active sites N* in the reactor is given by:

$$\frac{dN^*}{dt} = F_{in}^* - k_f N^* - N^* \frac{R_v}{V_p} \tag{16}$$

The molar flowrate of potential active sites into the reactor F^*_{in}. The volumetric flow rate of polymer from the reactor is R_v and the volume of the polymer phase in the reactor is V_p. Similarly, the following equations can be written for the number of moles of initiation sites N(0) and $N_H(0)$:

$$\frac{dN(0)}{dt} = k_f N^* - N(0)\left\{k_i[M] + k_{ds} + \frac{R_v}{V_p}\right\} \tag{17}$$

$$\frac{dN_H(0)}{dt} = Y(0)k_{fh}[H_2] + k_{fs}$$
$$-N_H(0)\left\{k_h[M] + k_{ds} + k_{hr}[AlEt_3] + \frac{R_v}{V_p}\right\} \tag{18}$$

Where

$$Y(0) = \sum_{r=1}^{2} N(r) = N(1) + N(2) \tag{19}$$

The population balance for living chains growing on active sites of length r = 1 is given by:

$$\frac{dN(1)}{dt} = k_i N(0)[M] + N_H(0)\{k_h[M] + k_{hr}[AlEt_3]\} +$$
$$Y(0)\{k_{fm}[M] + k_{fr}[AlEt_3]\} - N(1)\left\{k_p[M] + k_{fm}[M] +\right.$$
$$\left. k_{fr}[H_2] + k_{fr}[AlEt_3] + k_{fs} + k_{ds} + \frac{R_v}{V_p}\right\} \tag{20}$$

For the living chains with length greater than 1 the equivalent population balance is:

$$\frac{dN(2)}{dt} = k_p[M]N(1) - N(2)\left\{k_p[M] + k_{fm}[M] + k_{fh}[H_2] + k_{fr}[AlEt_3] + k_{fs} + k_{ds} + \frac{R_v}{V_p}\right\} \tag{21}$$

Population balances for dead chains (for r=2) are as follows:

$$\frac{dQ(2)}{dt} = N(2)\{[M]k_{fm} + [H_2]k_{fh} + [AlEt_3]k_{fr} + k_{fs} + k_{ds}\} - \frac{R_v}{V_p}Q(2) \tag{22}$$

The zeroth moment (number of chains) of the living polymer chain length distribution is:

$$\frac{dY(0)}{dt} = k_i N(0)[M] + N_H(0)\{k_h[M] + k_{hr}[AlEt_3]\} - Y(0)\left\{k_{fh}[H_2] + k_{fs} + k_{ds}(j) + \frac{R_v}{V_p}\right\}. \tag{23}$$

Mass balances on the first and second moments of the living polymer distribution are:

$$\frac{dY(1)}{dt} = k_i N(0)[M] + N_H(0)\{k_h[M] + k_{hr}[AlEt_3]\} + Y(0)\{k_{fm}[M] + k_{fr}[AlEt_3]\} + k_p[M]Y(0) - Y(1)\left\{k_{fm}[M] + k_{fr}[AlEt_3] + k_{fh}[H_2] + k_{fs} + k_{ds} + \frac{R_v}{V_p}\right\} \tag{24}$$

$$\frac{dY(2)}{dt} = \frac{d(\sum_{r=1}^{2} r^2\{N(r)\}}{dt} = k_i N(0)[M] + N_H(0)\{k_h[M] + k_{hr}[AlEt_3]\} + Y(0)\{k_{fm}[M] + k_{fr}[AlEt_3]\} + k_p[M]\{2Y(1) + Y(0)\} - Y(2)\left\{k_{fm}[M] + k_{fr}[AlEt_3] + k_{fh}[H_2] + k_{fs} + k_{ds} + \frac{R_v}{V_p}\right\} \tag{25}$$

$$\frac{dX(n)}{dt} = Y(n)\{k_{fm}[M] + k_{fr}[AlEt_3] + k_{fh}[H_2] + k_{fs} + k_{ds}\} - X(n)\frac{R_v}{V_p} \tag{26}$$

Where n=0, 1, 2.

The volumetric outflow rate of polymer, R_v, can be determined from the consumption rates of the monomers and the rate of change of the weight of polymer in the reactor:

$$R_v = \frac{M_w R}{\rho_s} - \frac{dB_w/dt}{\rho_s} \tag{27}$$

$$\frac{dB_w}{dt} = \frac{([M]_{in} - [M]) * M_w}{V_r * t} \tag{28}$$

Fogler (2004) monomer and hydrogen dynamic molar balances is written as:

$$\frac{d[M]}{dt} = -k_p[M]\left(\frac{2k_i f F_{in}}{k_{fm}}\right)^{0.5} \exp(-\frac{k_i}{2}t) \tag{29}$$

$$\frac{d[H_2]}{dt} = -k_p[H_2]\left(\frac{2k_i f F_{in}}{k_{fh}}\right)^{0.5} \exp(-\frac{k_i}{2}t) \tag{30}$$

Where *f* is the fraction of initiator free radicals successful in initiating chaining and has a typical value in the range 0.2 to 0.7.

Homopolymer Properties

The number average and weight average molecular weights, M_n and $M_{w,avg}$, can be determined using the method of moments as follows:

$$M_n = M_w\left(\frac{X(1)+Y(1)}{X(0)+Y(0)}\right) \tag{31}$$

$$M_{w,avg} = M_w\left(\frac{X(2)+Y(2)}{X(1)+Y(1)}\right) \tag{32}$$

The polydispersity Index (PDI) is defined by the ratio of weight average to number average molecular weights:

$$PDI = \frac{M_{w,avg}}{M_n}. \tag{33}$$

Control of MFI is an important for producing desired polypropylene grade. MFI of polymer is a function of its molecular weight, which is related to the operating conditions of the reactor and the feed composition. The relation between MFI and the weight average molecular weights of polypropylene is given by:

$$MFI = 3.346 * 10^{17} M_{w,avg}^{-3.472} \tag{34}$$

3.2.2. Model Solution

The operating conditions of a local petrochemical company as shown in Table 2 were used for this proposed model. The set of equations (16), (17), (18), (20) and (21) are stiff because the dynamics associated with changes in the intermediate species are very fast compared to the dynamics associated with the other states in the model. Therefore, Shamiri et al. [4] suggested converting the corresponding differential equations to algebraic equations by setting the left-hand-side derivative terms to zero.

Table 2. Operating Conditions of of a local petrochemical company.

Operating Conditions	
V_r(m^3)	31.87
T (°C)	72
P (Mpa)	3.2
Propylene (ton)	4.15
Catalyst (g)	50
Hydrogen (Mpa)	0.037
Production rate (ton)	2.5
Batch Time (hr)	4

The set of model equations were solved numerically using MATLAB by using Gauss elimination for linear algebraic equations and ode15s for ordinary differential equations.

4. Results and Discussions

Figure 1-4 shows the simulated weight average molecular weight, number average molecular weight, PDI and MFI as a function of time. The molecular weight of polymer determines major properties of the end product. Small variations in the molecular structure may improve or impair the polymer properties such as tensile strength, thermal stability, stiffness, hardness, softening point and impact strength considerably. The weight average molecular weight and the number average molecular weight show similar trends with an increase and a plateau at around 1.5 – 2.5 hrs.

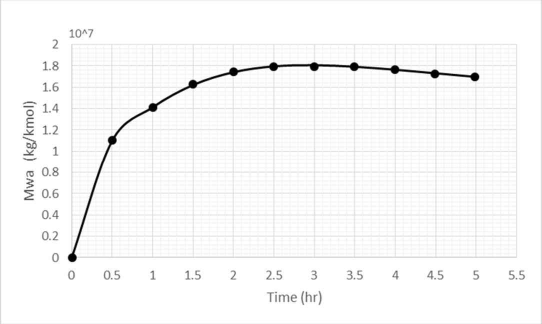

Figure 1. Weight Average Molecular Weight as a Function of Time.

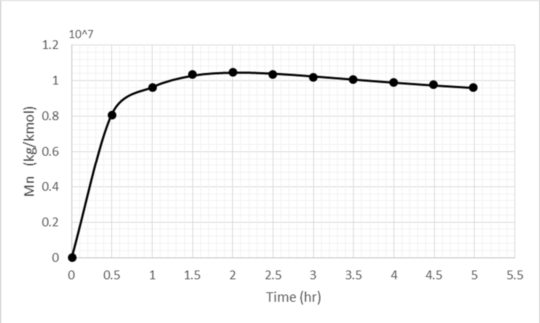

Figure 2. Number Average Molecular Weight as a Function of Time.

The PDI is used as a measurement of the breadth of the molecular weight distribution. The PDI value plateaus at around 3.5-4 hours.

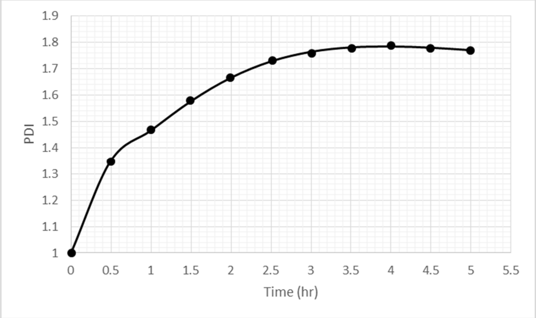

Figure 3. Polydispersity Index as Function of Time.

The most commonly used test or indicator for flow characteristic is the MFI, which offers an assessment of average molecular weight and is an inverse measurement of the melt viscosity. Knowing MFI of a polymer is vital to anticipate and control its processing. Figure 4 indicates a decreasing in MFI as the reaction proceeds. The local petrochemical company has a grade range of 1- 4, MFI starts to be within the range after an hour. At 4 hours it found to be 2.04. MFI is measured after the end of the batch run.

Actual batch runs which were collected from a local petrochemical company are presented in Table 3 along with the simulated results for MFI. To compare the predicted values with the monitored values, the residual plot (Figure 5) was used. It is clear that most of the MFI values are within +/- 20% of the simulated values except for 5 batch runs. The average absolute error, for all 15 batch runs, of 10.8 % was achieved. The error could be explained due to the slight variation in operating conditions, along their fixed set points, as a result of automatic control.

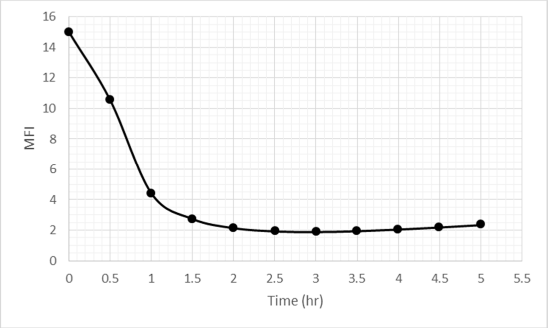

Figure 4. Melt Flow Index as Function of Time.

Table 3. Melt Flow Index of Several Batches from a local petrochemical company.

Batch	Time (hr)	MFI (Actual)	MFI (simulated)
1	4	2.86	2.04
2	4	2.24	2.04
3	4	2.01	2.04
4	4.5	2.21	2.177
5	5	2.32	2.33
6	4	2.03	2.04
7	4	2.65	2.04
8	4	2.01	2.04
9	4.58	2.44	2.18
10	4.5	2.13	2.177
11	5	2.26	2.33
12	4	1.82	2.04
13	5	1.58	2.33
14	4	1.87	2.04
15	4	1.83	2.04

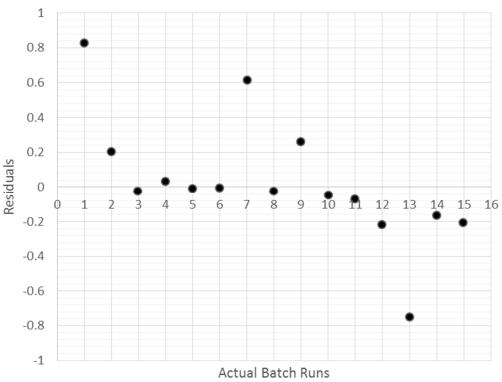

Figure 5. Residual Plot of MFI.

5. Conclusion

A mathematical model for the production of polypropylene in a batch reactor was developed in this study using MATLAB. It is shown that the model is able to predict the changes in number and weight average molecular weights, polydispersity index and melt flow index based on operating conditions of a local petrochemical company. The simulation shows similar trends to previous published work. The developed model was validated against actual collected batch runs of a local petrochemical company with an average absolute error of 10.8 %.

References

[1] Reusch, W. 2013, Polymers, 5th May, Michigan State University, Chemistry Department, viewed 27th November 2015, <https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm>.

[2] Fogler, HS 2004, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice-Hall, Inc. (Pearson Education, Inc.), New Jersey, USA.

[3] Villa, C. 2007, 'Reactor Modelling for Polymerization Processes', Industrial and Engineering Chemistry Research, vol46, issue 18, p. 5815-5823.

[4] Shamiri, A, Wong, SW, Zanil, MF, Hussain, MA Mostoufi, N 2015, Modified Two-Phase Model With Hybrid Control For Gas Phase Propylene Copolymerization In Fluidized Bed Reactors, Chemical Engineering Journal, Vol. 264, p. 706–719.

[5] Hatch, LF, Matar, S 1994, Chemistry of Petrochemical Processes, 2nd Edition, Gulf Publishing Company, United States of America.

[6] Choi, KY, Ray, WH 1985, The Dynamic Behaviour of Fluidized Bed Reactors for Solid Catalysed Gas Phase Olefin Polymerization, Chemical Engineering Science, Vol. 40, issue 12, p. 2261-2279.

[7] Meier, GB, Weickert, G, Pater, JTM and Westerterp KR 1999, The particle as microreactor: catalytic propylene polymerizations with supported metallocenes and Ziegler-Natta catalysts, Chemical Engineering Journal, Vol. 54, Issue 15-16, p. 3291-3296.

[8] McAuley, KB, Kaszas, G, Yao, KZ, Shaikh, S, Puskas, JE 2005, Kinetic simulation of living carbocationic polymerization. II. Simulation of living isobutylene polymerization using a mechanistic model, European Polymer Journal, Vol. 41, Issue 1, p. 1-4.

[9] Kiashemshaki, A, Mostoufi, N and Gharebagh, RS 2006, Two-phase modelling of a gas phase polyethylene fluidized bed reactor, Chemical Engineering Science, Vol. 61, Issue 12, p. 3997–4006.

[10] Rosenfeld, C, Serra, C, Brochon, C & Hadziioannou, G 2007, High-Temperature Nitroxide-Mediated Radical Polymerization In A Continuous Microtube Reactor: Towards A Better Control Of The Polymerization Reaction, Chemical Engineering Science, Vol. 62, Issues 18–20, p. 5245–5250.

[11] Ibrehema, AS, Hussaina, MA, Ghasemb, NM 2009, Modified mathematical model for gas phase olefin polymerization in fluidized-bed catalytic reactor, Chemical Engineering Journal, Vol 149, p. 353-362.

[12] Mil, R, Serrano, FL, Vargas, RO & Suastegui, LAM 2009, Emulsion polymerization process control, VI International Conference on Electromechanics and System Engineering, Mexico, p. 1-4.

[13] Mjalli, FS & Ibrehem, AS 2011, Optimal Hybrid Modeling Approach For Polymerization Reactors Using Parameter Estimation Techniques, Chemical Engineering Research and Design, Vol. 89, Issue 7, p. 1078–1087.

[14] Meng, W, Li, J, Chen, B and Li, H 2013, Modeling and Simulation of Ethylene Polymerization in Industrial Slurry Reactor Series, Chinese Journal of Chemical Engineering, Vol.21, Issue 8, p. 850–859.

[15] Lakatos, BG, Bárkányi, Á and Németh, S 2014, Three-Scale Modelling And Simulation Of A Batch Suspension Polymerization Vinyl Chloride Reactor, Computer Aided Chemical Engineering, Volume 33, p. 229–234.

[16] Huang, K Xie, R 2014, Modelling Of Molecular Weight Distribution Of Propylene Slurry Phase Polymerization On Supported Metallocene catalysts, Journal of Industrial and Engineering Chemistry, Vol. 20, Issue 1, p. 338–344.

[17] Weiss, ED, Jemison, R, Noonan, KJT, McCullough, RD, Kowalewski, T 2015,Atom Transfer Versus Catalyst Transfer: Deviations From Ideal Poisson Behaviour In Controlled Polymerizations, Polymer, Vol. 72, p. 226–237.

[18] Lima, NNM, Linan, LZ, Melo, DNC, Manenti, F, Filho, RM, Embiruçu, MMaciel, MRW 2015, Nonlinear Fuzzy Identification of Batch Polymerization Processes, Computer Aided Chemical Engineering, Vol. 37, p. 599–604.

[19] Yaghini, N Iedema, PD 2015, New Models Of Radical Polymerization With Branching And Scission Predicting Molecular Weight Distribution In Tubular And Series Of Continuous Stirred Tank Reactors Allowing For Multiradicals And Gelation, Chemical Engineering Science, Vol. 130, p. 301–309.