(RESEARCH ARTICLE)

CrossMark
click for updates

Simulation of continuous stirred tank reactor (CSTR) for polypropylene production

Kekpugile Kenneth Dagde [1], Gunorubon Jackson Akpa [2], Obarijimah Osaroworlu [3,*] and Olalekan Michael Adeloye [4]

[1] Professor, Department of Chemical/Petrochemical Engineering, Rivers State University, Port Harcourt.
[2] Professor, Department of Chemical/Petrochemical Engineering, Rivers State University, Port Harcourt.
[3] Master student, Department of Chemical/Petrochemical Engineering, Rivers State University, Port Harcourt.
[4] Doctoral student, Department of Chemical/Petrochemical Engineering, Rivers State University, Port Harcourt.

Abstract

This research study predicted the conversion and yield pattern for the polymerization of propylene to polypropylene. The polymerization process was performed using propylene as the monomer and ethylene as the co-monomer in a four continuous stirred tank reactor (CSTR) connected in series with a Ziegler-Natta catalyst. Model equations were developed for polypropylene polymerisation by applying the principle of conservation of mass in tandem with the rate equation. The resulting model equation was solved numerically using the Runge-Kutta fourth order method and a MATLAB program was written to implement the numerical techniques. The deduced model results depicted the conversion of propylene from the first reactor to the fourth reactor (0.9900 to 0.0113) and increase in polypropylene production as the reaction proceeds from the first reactor to the fourth reactor (0.0000 to 0.9878) showing the conversion and yield pattern of the process. The simulated model results were compared with literature data with a percentage deviation for polypropylene and propylene of 2.2% and 3.8% respectively.

Keywords: Propylene; Ethylene; Polypropylene; Polymerisation; CSTR In Series.

1. Introduction

Polypropylene as a thermoplastic polymer is used widely in variety of applications ranging from packaging, labelling, textiles such as ropes, thermal underwear and carpets, stationeries, plastic parts and re-usable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes [1] Propylene is a monomer for polypropylene production. Polymer is rugged and resistant to many chemical solvents, bases and acids [2]. Commercial polypropylene is isotactic and is crystalline for the low-density polyethylene (LDPE) and high density polyethylene (HDPE), hence useful as engineering plastic competing with materials such as acrylonitrile butadiene styrene (ABS)[3] Polypropylene is economical and translucent at uncoloured phase but is not as transparent as polystyrene, acrylic or certain other plastics, opaque or colour when pigmented, good resistance to fatigue. It has a range of melting point hence temperature can be gotten from a differential scanning colorimetric chart with perfect isotactic polypropylene having melting point of 171^0C (340^0F). Commercial isotactic polypropylene has a melting point that ranges from 160 to 166^0C (320^0F to 331^0F) depending on the atactic material and crystallinity. Syndiotactic polypropylene with a crystallinity of 30% has a melting point of 130^0C[1] Higher Melt Flow Rate of polypropylene fills plastic mold more easily during the injection or blow molding production process, and as higher melt flow rate increases, physical properties (impact strength) decreases. Revenues generated to exceed $145 billion ending of 2019 has cause polypropylene to be the second most important plastic as the demand for the material was growing at a rate of 4.4% per year between 2004 and 2012. The cracking of naphtha gives by-products such as propylene and ethylene and also the separation of fractional distillates gives ethylene, propylene, and lighter alkenes are obtained which is by-

product of ethylene. Propylene does not occur naturally, but obtained from the thermal and catalytic cracking of petroleum and natural gas product together with other aromatic hydrocarbons such as benzene, toluene, and xylene [4] In the laboratories, propylene is prepared by the method of dehydrogenation and alkyl-halides. Polypropylene is a tonnage polymer with growth rate higher than norm due to wide range of applications[2] Three types exist: Homo-polymer (general purpose grade used in variety of different applications); block copolymers (incorporates 5-15% ethylene much improved impact resistance extending to temperature of below -20^{0}C and become more tougher further, enhanced by impact modifiers); and elastomers in a blending process and random copolymers (incorporated co-monomer units arranged randomly along the polypropylene long chain molecule and polymer typically contains 1-7% ethylene is selected where a lower melting point, more flexibility and enhanced clarity are advantageous)[5] Co-monomer is combination of ethylene-propene rubber or EPPM added and polypropylene homopolymer to increases low temperature impact strength. Randomly polymerized ethylene monomer combined with polypropylene homopolymer leading to decrease in the polymer crystallinity, lowers the melting point and makes the polymer more transparent [6]

Polypropylene production is aimed at solving material and environmental problems in Nigeria, and as a useful polymeric product for vast applications such as packaging and labelling, textiles (such as ropes, thermal underwear and carpets), stationeries, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. Based on its wide applications, economic production of polypropylene will replace the dependence on metallic material thus, the needs to develop a model that predicts polypropylene yield in an isothermal continuous stirred tank reactor (CSTR) in series. This research study shall involve development of model equations for polypropylene production from first principle with its rate equation, numerical solution of model equations using the Runge-Kutta 4th order algorithm and a MATLAB program, comparison and validation of simulated results and analysis of the effects of operating parameters on the conversion and yield of polypropylene.

2. Material and methods

Polypropylene manufacturing process is made up of a raw material: for refining process, polymerization process, catalyst deactivation process and granulation process. Raw material refining process is an upstream process used for eliminating minute amounts of impurities that affect the process such as water, oxygen, carbon monoxide, carbon dioxide, carbonyl sulphide etc., called impurities from the propylene, other monomers, solvents, other raw materials and auxiliary materials needed for the essential purification of the raw materials. Process is set up at a raw material manufacturing plant sited upstream of the polypropylene manufacturing plant and for the process stabilization of the entire plant.[7] The polymerization process is the addition of monomers growing from propylene and, if necessary, ethylene and other monomers into contact with a catalyst suitable for polymerization activity. Most industrial catalysts are granular mostly in the form of secondary or tertiary particles of several tens of μm sized and molecules having diameters of several hundred angstroms [8] The polymerization reaction occurs at the active sites of the catalyst particles, and the polypropylene formed precipitates out thereby allowing the catalyst to splits into primary particles. There are few deviations in the shape of the catalyst and forms polypropylene particles that resemble the original aggregated catalyst shape [9] The deactivation process eliminates catalyst residue, the solvent and atactic polymers, components unnecessary from the polypropylene particles obtained during the polymerization process. The operation for eliminating the catalyst is deashing. Solvent in the polymerization process is used for recovering and purifying process. Granulation process as the last downstream is a process for melting and kneading additives and fillers into the polypropylene particles that have undergone the post processing and forming pellets [10]
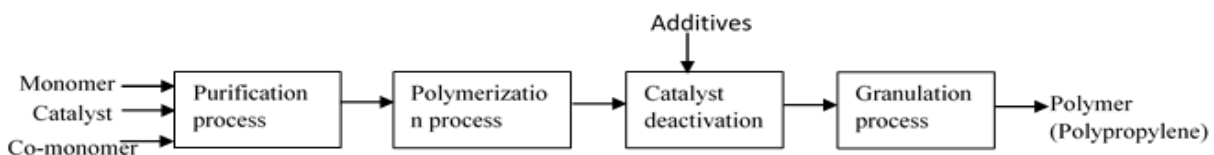
Figure 1 Polpropylene Polymerisation process

2.1. Model Development

The polymerization process occurring in the reactor can be broken down into chemical reaction, transfer of mass, and heat. The modelling of the reactor for the polymerization reaction will therefore, be based on the equations describing the phenomena such as the reaction rate equation, continuity equation and energy balance equation.

2.2. Model Assumptions

In carrying out this research study, the following assumptions were made.

The liquid content of the reactor should be perfectly mixed by an agitator (stirrer). Thus, the density of the mixture is constant throughout the reactor.

An isothermal operational process is considered, hence, energy balance is neglected since there is no temperature change in the process.

Fresh catalyst and co-catalyst goes to the first reactor only, reactor volume and reactor flow rates are constant.

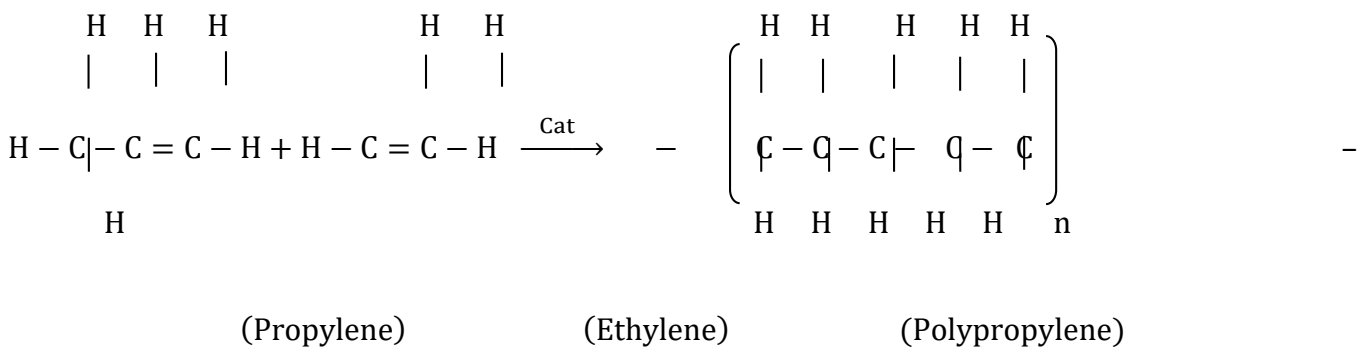Momentum does not change under the operating condition.

2.3. Continuous Stirred Tank Reactor in Series

In modelling the polymerization process of polypropylene using four continuous stirred tank reactors in series with each reactor receiving liquid and vapour recycled from the overhead condenser. However, it is assumed that only the first CSTR receives fresh catalyst and co-catalyst with constant temperature and constant pressure for all the reactors.
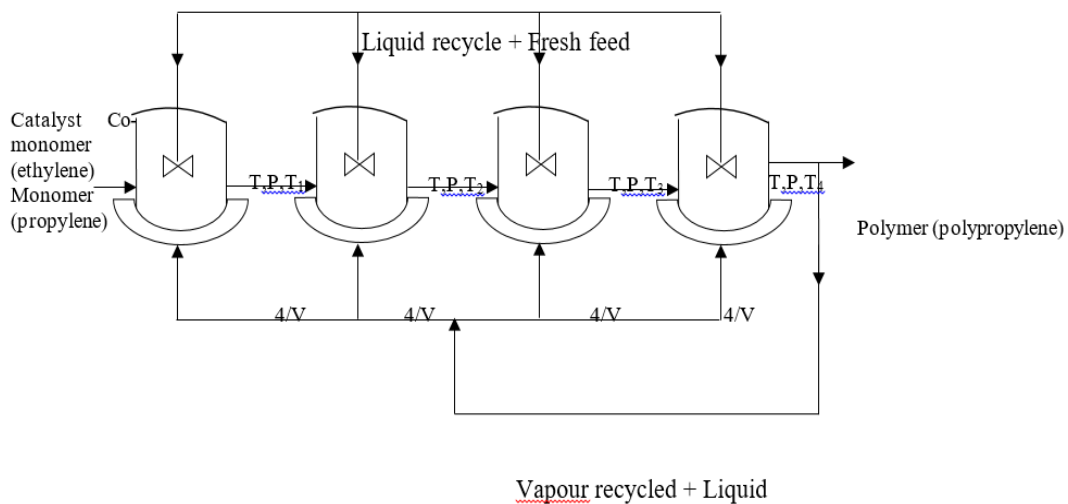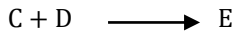

Figure 2 Continuous Stirred Tank Reactors in series.

The chemical reaction equation for the polymerization process is thus.

$$
\begin{array}{c}
\overset{\text{H\quad H\quad H}}{\underset{\text{H}}{\overset{|\quad|\quad|}{H-C-C=C-H}}} + \overset{\text{H\quad H}}{\overset{|\quad|}{H-C=C-H}} \xrightarrow{\text{Cat}} -\left[\overset{\text{H\quad H\quad\quad H\quad H\quad H}}{\underset{\text{H\quad H\quad H\quad H\quad H}}{\overset{|\quad|\quad\quad|\quad|\quad|}{C-C-C-C-C}}} \right]_n -
\end{array}
$$

(Propylene)   (Ethylene)   (Polypropylene)

The polymerisation reaction process can be represented hypothetically as

$$C + D \longrightarrow E$$

Where C is propylene, D is ethylene and E is the polypropylene.

The fundamental dependent quantities for the reaction are total mass of reaction mixture in the reactor, the mass of the component in the reacting mixture and product, and the total energy of the reacting mixture in the tank. The momentum of the CSTR in series does not change under any operating condition for the reaction, thus, it is neglected.

2.4. Rate Equation

A simplified rate equation as proposed by Shariati 1996 is adapted and will be used in this work[11] This equation is given as follows;

$$(-r_i) = R_p = K_p C^*[M] \qquad\qquad 1$$

Where R_p is the proportional rate, K_p is the rate constant, C^* the total number of active site and $[M]$ is the monomer concentration and C^* and $[M]$ are of first order

2.5. Continuity Equation

A model equation can be used to predict process interactions with various input parameters and investigate operational process behaviour. The law of conservation of mass for reacting component is applied to each reactor above as follows;

$$\begin{bmatrix} Rate\ of\ accumulation \\ of\ substance\ within \\ the\ system \end{bmatrix} = \begin{bmatrix} Rate\ of\ inflow \\ of\ substance \\ into\ the\ system \end{bmatrix} - \begin{bmatrix} Rate\ of\ outflow \\ of\ substance \\ out\ of\ the\ system \end{bmatrix} \pm \begin{bmatrix} Rate\ of\ substance \\ generated/disappearance \\ within\ the\ system \end{bmatrix}$$

2.6. Component Mass Balance

The general mass balance equation is expressed for species i as:

$$\begin{bmatrix} Rate\ of\ accumulation \\ of\ component\ i\ in \\ the\ system \end{bmatrix} = \begin{bmatrix} Rate\ of\ input \\ of\ component\ i \\ into\ the\ system \end{bmatrix} - \begin{bmatrix} Rate\ of\ output \\ of\ component\ i \\ from\ the\ system \end{bmatrix} \pm \begin{bmatrix} Rate\ of\ generated/ \\ disappearance\ due\ to \\ chemical\ reaction \end{bmatrix} \qquad 2$$

Thus,

$$\begin{bmatrix} Rate\ of\ accumulation \\ of\ component\ i\ in \\ the\ system \end{bmatrix} kg/time = \frac{dy_i m_i}{dt} = \frac{dy_i \rho_T V}{dt} \qquad\qquad 3$$

$$\begin{bmatrix} Rate\ of\ input \\ of\ component\ i \\ into\ the\ system \end{bmatrix} kg/time = y_{io} m_{To} = y_{io}\rho_T F_o \qquad\qquad 4$$

$$\begin{bmatrix} Rate\ of\ output \\ of\ component\ i \\ from\ the\ system \end{bmatrix} kg/time = y_i m_T = y_i \rho F \qquad\qquad 5$$

$$\begin{bmatrix} Rate\ of\ generated/ \\ disappearance\ due\ to \\ chemical\ reaction \end{bmatrix} kg/time = (-r_i)V M_W \qquad\qquad 6$$

Where: ρ_T (kg/m³) is the density of substance, m_i(kg) is the mass of individual component, $V(m^3)$ is the volume of reactor, y_i (mol/m³) is the concentration of individual component, F (m³/time) is the volumetric flow rate, M_W (kg/mol) is the molecular weight of component, and $(-r_i)$ is the rate constant, τ is residence time, m_i is mass of individual component and m_T is total mass of component

17

Substituting equations 1, 3, 4, 5, 6 into equation 2 for constant density, volume and volumetric flow rate and algebraic analysis yields

$$\frac{dy_i}{dt} = \frac{F}{V}(y_{io} - y_i) - K_P C^* y_i \qquad 7$$

Equation 7 is the model equation for the flow of component i in any of the reactors.

Therefore, the general model equation for any components and four CSTR reactors in series can be written as
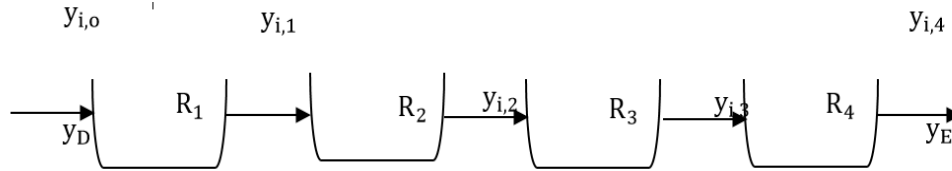
Figure 3 CSTR's in series for reactants and product

$$\frac{dy_{i,j}}{dt} = \frac{F}{V}(y_{i,j-1} - y_{i,j}) - K_P C^* y_{i,j}$$

Where i is the components and j stands for number of reactor

2.7. Determination of Operating Parameter

M_c = mass of catalyst used =15.3kg(co-catalyst) + 16.3kg (main catalyst) = 31.3kg

$$\therefore y_{Co} = \frac{M_{Co}}{M_{Co} + M_{Do}} = 0.98 \quad \text{and} \quad y_{Do} = \frac{M_{Do}}{M_{Co} + M_{Do}} = 0.01$$

Table 1 Operating Parameters [12]

Names of species	Symbol	Value
Mass of potential active site	C*	2.23mols
Propagation constant	K_P	0.0132mols/sec
Volume of CSTR	V	6.624m³
Mass of ethylene into the reactor	M_{DO}	0.2 tons
Mass of propylene into the reactor	M_{CO}	19.2 tons
Mass of polypropylene produced	M_{Eo}	17.9 tons
Heat of reaction	ΔH_r	-69KJmol⁻1
Volumetric flow rate	F_o	0.33685 m/sec
Mass of main catalyst	M_{mc}	16.3kg
Mass of co-catalyst	M_{cc}	15kg
Mass of catalyst used	Mc	31.3kg
Mass fraction of propylene used	y_{Co}	0.99
Mass fraction of ethylene used	y_{Do}	0.01
Step size	H	0.01
Residence time	t_s	120sec

2.8. Solution Techniques

The model equations developed yielded a set of first order ordinary differential equations that were solved numerically using the fourth order Runge-Kutta Algorithm method[13] Also, MATLAB program shall be developed and used to obtain all the required results and graphs.

3. Results and discussion

Table 2 shows that the mass fraction of propylene started at an initial state of 0.9900 and reduced to 0.6270 as the reaction proceeds at the end of the first reactor, while the mass fraction of polypropylene started at 0.0000 and increased to 0.3730 at the end of the first reactor. This process continues for the second, third and fourth CSTR until the final product is formed. Also, Table 3 shows the validation of the result obtained using matrix laboratory (MatLab) with literature data [14]. As can be deduced from Table 3, the deviation of Polypropylene composition with literature data is -2.2% and composition of propylene conversion deviate as -3.8% respectively.

Table 2 Model Results Showing the Rate of Conversion of Propylene to Polypropylene

I	N	Yci(I,N)	Yd(I,N)	Ye)(I,N)
1	0	0.9918	0.0000	0.0000
1	1	0.7623	0.0000	0.2430
1	2	0.6691	0.0000	0.3266
1	3	0.6422	0.0000	0.3560
1	4	0.6341	0.0000	0.3660
1	5	0.6281	0.0000	0.3711
1	6	0.6271	0.0000	0.3723
1	7	0.6263	0.0000	0.3728
1	8	0.6260	0.0000	0.3728
1	9	0.6260	0.0000	0.3728
1	10	0.6251	0.0000	0.3728
1	11	0.6251	0.0000	0.3731
1	12	0.6251	0.0000	0.3731
1	13	0.6251	0.0000	0.3731
1	14	0.6251	0.0000	0.3731
1	15	0.6251	0.0000	0.3731

Table 3 Simulation Validation

| Parameter	Model prediction	Literature data	%Deviation
polypropylene composition	0.37	0.45	-2.2
propylene composition	0.40	0.55	-3.8
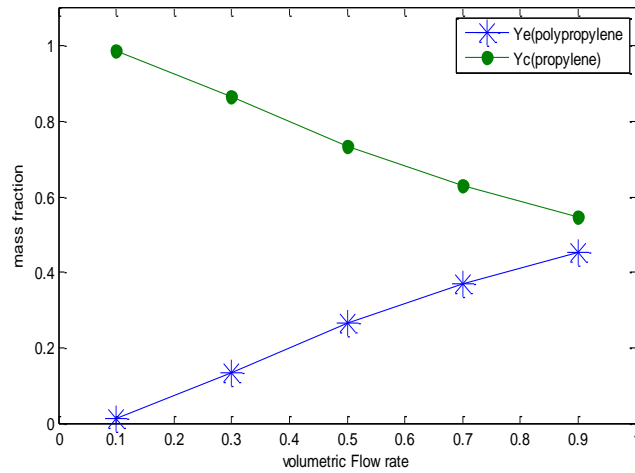
Figure 4 Variation of mass fraction with volume of the reactor

Figure 4 depicts the investigation of volumetric flow rate influence on propylene conversion to polypropylene. An increase in the volumetric flow rate results in an increase in the amount of polypropylene produced along the reactors in series while propylene is being consumed in the series reactor.

As shown in Figure 5, increase in the reactor volume leads to more time for monomers conversion, that is increase in the residence time or reaction time, thereby resulting in an increase in the conversion of propylene as the reaction proceeds from the first reactor to the fourth reactor (a decrease in mass fraction of propylene) and corresponding increase in the yield of polypropylene
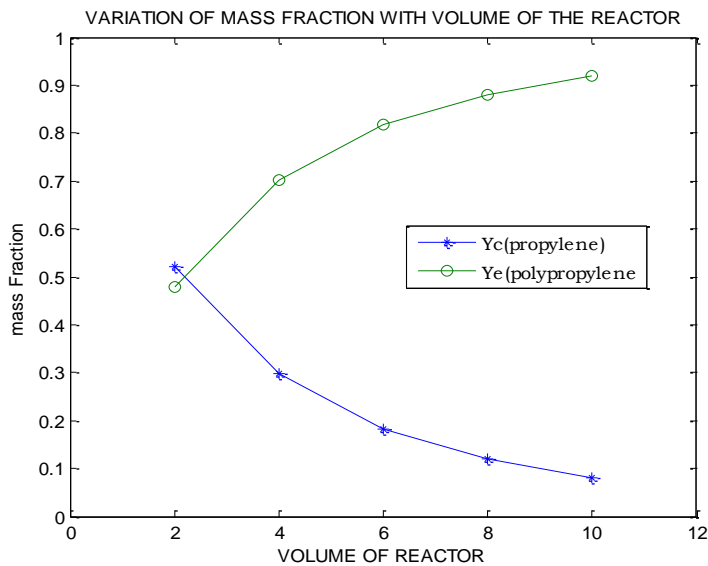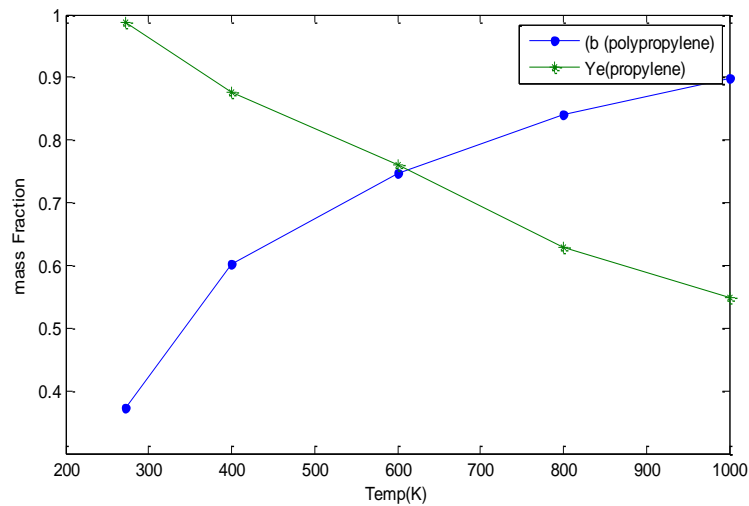

Figure 5 Variation of mass fraction with volume of the reactor

.
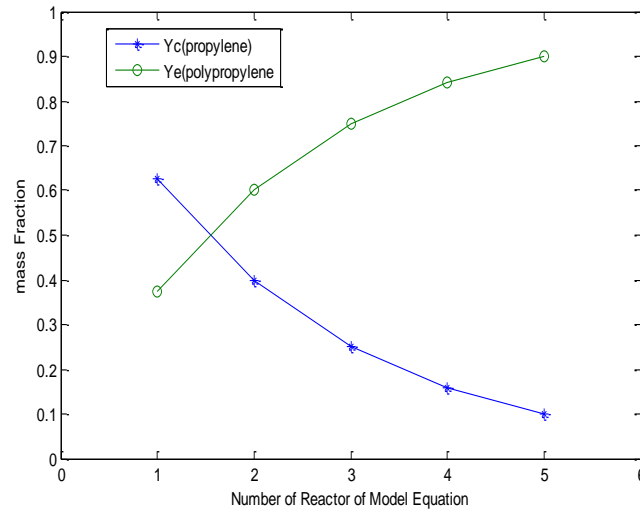
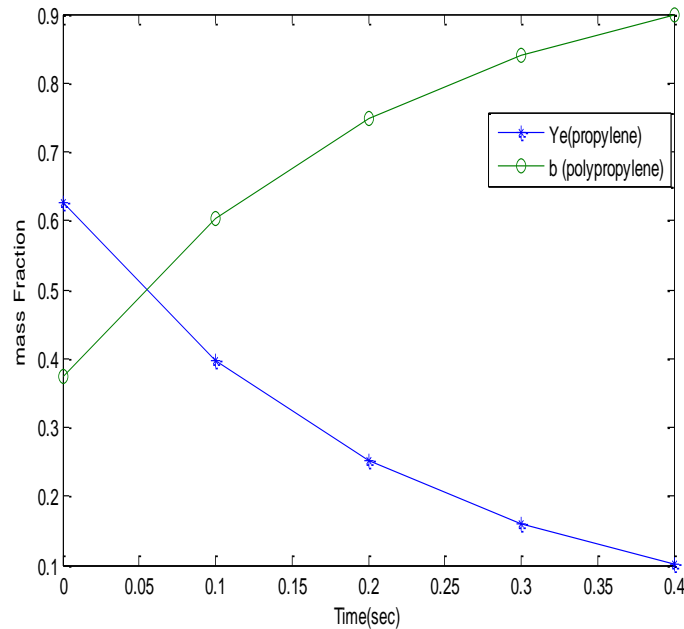**Figure 6** Variation of mass fraction with number of reactors

Figure 6 shows the effects of the number of reactors on the conversion of propylene to polypropylene. Hence, an increase in the number of reactor will lead to an increase in the total number of volume of the process. As the number of reactors increase for a particular volume, the mass fraction of propylene decreases, that is propylene conversion to polypropylene increases. The yield of polypropylene increase sharply but it should be noted that the economics of the polymerization process will have major effects on the number of reactors in series in tandem with polypropylene yield.

Figure 7 Variation of mass fraction with temperature

From Figure 7 as temperature increases, the mass fraction of polypropylene increases indicating that the polypropylene is been formed while mass fraction of propylene decreases due to its conversion to polypropylene. Hence, temperature increase favours the rate of production of polypropylene.

Figure 8 Variation of mass fraction with time

Reaction time or residence time is of importance in production process especially in a CSTR as the time the feed spent in the reactor will determine the yield of the process. As shown in Figure 8, as reaction time increases, the production rate of polypropylene increases until at a point at which the process will be constant with a corresponding decrease or reduction in propylene mass fraction.

4. Conclusion

The model for four continuous stirred tank reactor connected in series for the polymerization of propylene has been developed and simulated using the principle of conservation of mass. The developed model equations have been solved numerically using the Runge-Kutta 4th order algorithm with the aid of MATLAB program that implement the numerical solution technique. The model result shows the trend of the conversion and yield pattern of propylene to polypropylene.

Compliance with ethical standards

Acknowledgments

Disclosure of conflict of interest

We (Dagde, K. K., Akpa, J. G., Osaroworlu, O, and Adeloye, O. M) the authors of the article "Simulation of Continuous Stirred Tank Reactor (CSTR) for the Production of Polypropylene" wish to state that there are no conflicts of interest in this our research article.

References

[1]   Sh, A., Maier, R. D., & Bidell, W. 2016. Polypropylene: Gas Phase Polymerization and Reactor Blends. New York: Elsevier. DOI: 10.1016/B978-0-12-803581-8.03757-7

[2]   Bikiaris, D. N,*Microstructure and Properties of Polypropylene/Carbon Nanotube Nanocomposites. Materials* 2010; 3:2884–2946.

[3]   Panneerselvam, K. & Lenin, K. Parameters Optimization in FSW of Polypropylene Based on RSM. *Multidiscipline Modeling in Materials and Structures,* 2015; *11*(1):32-40.

[4]   Khan, M. J. H., Hussain. M. A., Mansourpour, Z., Mostoufi, N., Ghasem, N. M., & Abdullah, E. C. CFD Simulation of Fluidized Bed Reactors for Polyolefin Production—A Review. *J. Ind. Eng. Chem.*, 2014; 10(6):14-20.

[5]   Kennedy, J. F., & Knill, C. J. 1992 Multicomponent Polymer Systems; Miles, I.S., Rostami, S., Eds.; Longman Scientific & Technical: Harlow, UK, 435.

[6]   Islam, M. A., Hussein, I. A., & Atiqullah, M. Effects of Branching Characteristics and Copolymer Composition Distribution on Non-Isothermal Crystallization Kinetics of Metallocene LLDPEs. *Eur. Polym. J.* 2007; 4(3):599–610.

[7]   Aktaş, N., Boyacı, İ. H., Mutlu, M., & Tanyolaç, A. Optimization of Lactose Utilization in Deproteinated whey by Kluyveromyces Marxianus using Response Surface Methodology (RSM). Bioresource Technology, 2007; 9(18):2252–2259.

[8]   Balow, M. J. 2003. *Handbook of Polypropylene and Polypropylene Composites*; CRC Press: New York, NY, USA.

[9]   Ibrehem, A. S., Hussain, M. A., & Ghasem, N. M.Modified Mathematical Model for Gas Phase Olefin Polymerization in Fluidized-Bed Catalytic Reactor. *Chem. Eng. J.* 2009; 14(9):353–362.

[10]   Hafiz, A., Ahmadpour, A., Koolivand-Salooki, M., Heravi, M. M., & Bamoharram, F. F. Comparison of rsm and ann for the Investigation of Linear Alkylbenzene Synthesis Over H14 [NaP5 W30O110]/SiO2 catalyst. *J. Ind. Eng. Chem.*, 2013; 1(9):1981–1989.

[11]   Shariati, A. 1996. Kinetic Modelling of Slurry Polymerisation of Ethylene with a Polymer Supported Ziegler-Natta Catalyst. Ph.D Thesis, Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

[12]   Neeraj, P. K., Bruce, L., Kevin, C. S., Liu, Y. A., Ashuraj, S., Sundaram, R., Simon, L., Yuhua, S. & Chau-Chyun, C. Steady State and Dynamic Modeling of Gas Phase Polypropylene Processes using Stirred Bed Reactors. *Ind. Eng. Chem. Res,* 2004; *43* (4):892-895

[13]   Kreyzig, E. 2002. *Advanced Engineering Mathematics,* 8th Edition, John Wiley and Sons,

[14]   Dagde, K. K., & Shadrach, C. N. Computer Aided Design of Fluidized Bed Reactor for Production of Polypropylene *Journal of Energy Technology and Policy,* 2018; 10(3):2224-3222