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By Devika P.D Ashwini K. Agrawal Dinesh P.A & Rama Krishna Prasa

Jawaharlal Nehru Technological University

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Non-Linear Mathematical Modelling of Nylon-6 Polymerization Reactors

Devika P.D ^α Ashwini K. Agrawal ^σ Dinesh P.A ^ρ & Rama Krishna Prasad ^ω

Abstract- Investigations on nylon-6 polymerization reactors such as VK (Vereinfacht Kontinuierliches Rohr) tube (vertical column) reactors have been explored to a very limited extent owing to their complex internal structure, which leads to uncertain velocity profile of the reactants inside the reactor. However, usually a flat velocity profile (plug flow profile) of reaction mixture is assumed inside the reactor leading to large errors in prediction of final properties of the product. In the current study, a modified simulation model has been developed for the Nylon-6 polymerization using mono acid stabilizers (acetic acid) in an industrial VK tube reactor. The variation of the velocity profile, which may result in axial changes of concentrations of different reactants along the length of the reactor has been accounted for by considering a small value non-linear time dependent decaying function. The model fetched significantly better results than the earlier model with plug flow profile of the reactants²⁴. The pattern of the concentration profiles of conversion, molecular weight and the end groups were found to be similar in the two cases, however, the results on end-group concentrations and the molecular weight of the final polymer were predicted to be much closer to the actual industrial data for the simulated reactor. This model can be very useful in the process optimization and in the designing of new VK tubes for increased productivity.

Keywords: Nylon-6 polymerization, VK tube reactors, modelling and simulation, optimization.

I. INTRODUCTION

VK (Vereinfacht Kontinuierliches Rohr) column reactor is one among the most well known reactors used for the hydrolytic polymerization of ϵ -caprolactam. Vertical tube reactors are designed using the internal gratings to achieve the equal heating and close uniform flow (i.e. flat velocity profile). In literature²⁴, raw materials, viz., ϵ -caprolactam, water and acetic acid are passed freely at the reactor entrance.

The velocity profile of the feed seems to be one more important parameter in controlling the rate of reactions in the model in addition to the pressure, temperature, and water concentration. Work on modelling and simulation of such reactors is scanty due to their complicated reactor configuration and lack of industrial data.

Author ^α ω: Jawaharlal Nehru Technological University, Hyderabad, 500 085, India

Author ^σ: Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi, 110 016, India.

e-mail: ashwini@smiitd.com

Author ^ρ: M. S. Ramaiah Institute of Technology, MSRIT Post, Bangalore 560 054, India. e-mail: dineshdp@msrit.edu

Many models were developed to study of the significance of H₂O elimination in the polymer mixture in a tubular reactor by different authors^{5,11,16-19}. Recently, we reported²⁴ the result of hydrostatic pressure within the reacting system using a plug flow velocity profile. The model predicted M_n, NH₂ and COOH concentrations with higher accuracy compared to the other models reported in the literature. However, the non-linear time dependent effects of induced velocity profile due to the internal structure of the reactor could not be incorporated in this model. The industrial VK tube reactors used for nylon-6 polymerization are very complex and it is extremely difficult to include actual velocity profiles of the reactants inside the reactors.

In the current study, a simulation model has been developed for Nylon-6 polymerization with mono acid stabilizers in a VK tube reactor. The axial changes of concentrations of various reaction components down the length of the reactor have been simulated by considering the non-linear time dependent decaying factor for each reactant species.

II. MODEL OF VK TUBE REACTOR WITH CORRECTION FOR VELOCITY PROFILE

The VK tube reactor that was modelled has five independent portions. The temperatures in the reaction mixture were measured by the thermocouple wells at six places. Figure 1A represents the schematic representation of the VK tube reactor. Input consisting of molten caprolactam, mono functional acid and water was passed to the entrance of the VK tube under a nitrogen cover. A water seal was kept above the reactor to allow the purged nitrogen to escape. The heat exchanger 1 (HE-1) heated the reaction mixture in zone-1 as it passes through HE-1. The melt in zone-3 upper and lower was heated by the heating jackets and the exothermic reactions. The temperature of the polymer mixture slowly increased from the top layer to the centre portion until the temperature reached the maximum point. Another heat exchanger was used to decrease and stabilize the temperature towards the bottom of the reactor. The end products such as unreacted caprolactam and the polymer were collected from the bottom of reactor.

In our earlier work²⁴, feed to the VK tube reactors were considered to be flowing normally (that is with no velocity profile), which might not be realistic.

However, in the present work, the flow of reactants was assumed to have a mild and possibly an irregular velocity profile caused by the shear forces exerted in the reactor walls and gratings in the upward direction and the gravitational force in the downward direction. Therefore, our earlier model²⁴ was modified to incorporate non-linear time dependent effect on the reaction mixture (monomer (m), W, P, and acetic acid (P_{1x})). Considering the geometry of the reactor to be symmetrical, an empirical non-linear time dependent exponential quantity given by equation (1) has been included in the mass balance equations of the reaction components. These modified mass balance equations which are of first order non-linear ordinary differential equations type (Table 2) have been solved by using the fourth order Runge-Kutta numerical method for the concentrations of all the species in the reaction scheme.

Quantity of reaction species changed due to the faster or slower velocity of the species 'i' compared to the average velocity profile of the reaction mixture is given as

$$= \alpha_i \exp(\beta_i t) \text{ moles/kg/h.} \quad (1)$$

where α_i and β_i are the parameters to be fitted for each species 'i' so that the output polymer properties match well with the industrial data.

a) Determination of water concentration

As mentioned in our previous work²⁴ the following vapour liquid equilibrium equation which is selected after testing several vapor liquid equilibrium equations^{11,20,21} was used in the model to find the water quantity in the polymer mass in the vaporizing zone of the reactor.

$$[W] = 10^{-2} P_T \exp(8220/T - 24.36) \quad (2)$$

The given relation was used to determine the amount of water that was retained in the reaction mixture at each point in the reactor in the vaporizing zone. For the modified model with pressure effect and the non-linear time dependent adjustment of the concentration, the above equation was modified as given below.

$$[W] = 10^{-2} P_T \exp(8220/T - 24.24) + \alpha_4 \exp(\beta_2 t) \quad (3)$$

Where P_T is the total pressure in pascals given by

$$P_T = P_A + 9.81 (\rho_W H_W + \rho_M H_P) \quad (4)$$

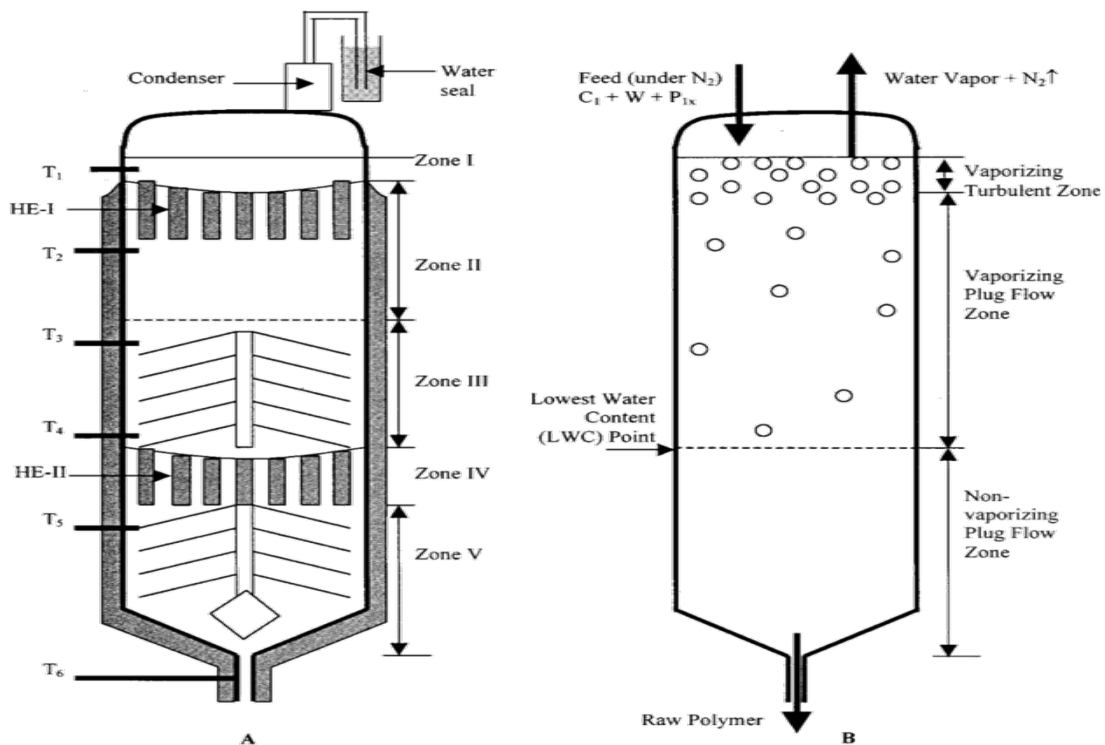


Figure 1: VK Tube Reactor

Where P_A is the atmospheric pressure given by 1.013×10^5 Pa. The original atmospheric pressure (P_A) at the industrial place was 2% lower than P_A and hence the change from 24.36 to 24.24 in Equation (2). α_4 and β_2 are the factors to be adjusted to fit the industrial results and to get the quantity of water consumed/produced in moles/kg/h, representing the non-linear time dependent influence of the velocity on the water concentration. The

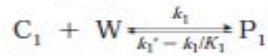
value of $[W]$ was calculated using Equation (3) at all the points in the top portion of the tube. In the non-vaporizing zone, i.e., from the LWC point downward, the total water in the reaction mass and in the product was assumed to be a constant. Therefore the value of $[W]$ is calculated using a mass balance equation.

$$[W] + [P] = [W_{CP}] + [P_{CP}] \quad (5)$$

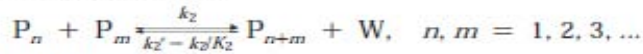
where $[P]$ is moles/kg of Nylon-6 near the interested point and $[W_{CP}]$ and $[P_{CP}]$ are moles/kg of H_2O and Nylon-6 at the lowest water content location.

Table 1: Kinetic Scheme for Nylon 6 Polymerization

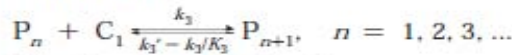
1. Ring-Opening



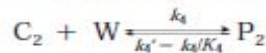
2. Polycondensation



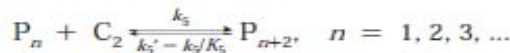
3. Polyaddition



4. Ring Opening of Cyclic Dimer



5. Polyaddition of Cyclic Dimer



6. Reaction with Monofunctional Acid

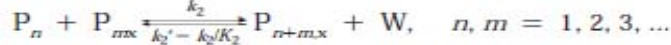


Table 2: Mass Balance Equations with Induced Input to the Top of the Reactor

$$\frac{dm}{dt} = -k_1mw + k_1'p - k_3m\lambda_0 + k_3'(\lambda_0 - p) + \alpha_1 \exp(\beta_1 t)$$

$$\frac{dp}{dt} = \begin{cases} k_1mw - k_1'p - 2k_2p\lambda_0 + 2k_2'mw(\lambda_0 - p) - k_3pm + k_3'p - k_2\lambda_{0x}p + \\ k_2'w(\lambda_{0x} - p_{1x}) - k_5pc_2 + k_5'p + \alpha_2 \exp(\beta_1 t) \end{cases}$$

$$\frac{d\lambda_0}{dt} = k_1mw - k_1'p - k_2\lambda_0^2 + k_2'w(\lambda_1 - \lambda_0) - k_2\lambda_0\lambda_{0x} + k_2'w(\lambda_{1x} - \lambda_{0x}) + k_4wc_2 - k_4'p$$

$$\frac{d\lambda_1}{dt} = \begin{cases} k_1mw - k_1'p + k_3m\lambda_0 - k_3'(\lambda_0 - p) - k_2\lambda_{0x}\lambda_1 - k_2'w(\lambda_{1x} - \lambda_{2x})/2 + \\ 2k_5c_2\lambda_0 - 2k_5'(\lambda_0 - 2p) + 2k_4wc_2 - 2k_4'p \end{cases}$$

$$\frac{d\lambda_2}{dt} = \begin{cases} k_1mw - k_1'p + 2k_2\lambda_1^2 + k_2'w(\lambda_1 - \lambda_3)/3 + k_3m(\lambda_0 + 2\lambda_1) + \\ k_3'(\lambda_0 - 2\lambda_1 + p) - k_2\lambda_2\lambda_{0x} + k_2'w(2\lambda_{3x} - 3\lambda_{2x} + \lambda_{1x})/6 + 4k_5c_2(\lambda_1 + \lambda_0) + \\ 4k_5'(\lambda_0 - \lambda_1 + p) + 4k_4wc_2 - 4k_4'p \end{cases}$$

$$\frac{dc_2}{dt} = -k_4c_2w - k_4'p - k_5c_2\lambda_0 + k_5'(\lambda_0 - 2p)$$

$$\frac{d\lambda_{1x}}{dt} = k_2\lambda_1\lambda_{0x} - k_2'w(\lambda_{2x} - \lambda_{1x})/2$$

$$\frac{d\lambda_{2x}}{dt} = k_2(2\lambda_1\lambda_{1x} + \lambda_2\lambda_{0x}) - k_2'w(4\lambda_{3x} - 3\lambda_{2x} - \lambda_{1x})/6$$

$$\frac{dp_{1x}}{dt} = -k_2p_{1x}\lambda_0 + k_2'w(\lambda_{0x} - p_{1x}) + \alpha_3 \exp(\beta t)$$

Table 3: Polynomial Expressions for the Constants (Magnitudes & Amplitudes) Used in the Non Linear Time Dependent Functions Incorporated in the Mass Balance Equations of the Various Reaction Species

Expressions For The Magnitudes And Amplitudes Terms*	Best Fit Values In The Present Model		
	Data 1 T=11.71 Hrs	Data 2 T=14.5 Hrs	Data 3 T=15.17 Hrs
$A_1 = 0.00197T^2 - 0.058397T + 0.433939$	0.02	0.001	0.001
$A_2 = -0.002485T^2 + 0.06476T - 0.42068$	-0.003	-0.004	-0.01
$A_3 = 0.0001T^2 + 0.0001T + 0.01$	0.01	0.01	0.01
$A_4 = -0.000207T^2 + 0.00615T - 0.05057$	-0.007	-0.005	-0.005
$B_1 = 0.0001T^2 + 0.0001T - 0.001$	-0.001	-0.001	-0.001
$B_2 = 0.0001T^2 + 0.0001T + 0.001$	+0.001	+0.001	+0.001

* T = total polymerization time

b) Kinetic Model

The reaction model of nylon-6 polymerization has been presented in Table 1. The previous model rate equations²¹ for different species were modified to incorporate the non-linear time dependent factor for the various species and are presented in Table 2. The major reactions included in the reaction model in nylon-6 polymerization were ring opening, poly-condensation and poly-addition. The production of cyclic oligomers were accounted by the ring opening and poly-addition reactions of cyclic dimer (C_2) in the process. Higher order cyclic oligomers were neglected to make the analysis easy. The kinetic scheme includes the reactions involving a mono functional acid such as acetic acid and the reactions were catalysed by the carboxyl end groups of the mono functional acid. The rate constants for all the reactions were estimated by the values of kinetic data determined from experimental work^{2,3,5}.

The constants, α and β , which are magnitudes and amplitudes of the nonlinear time dependent functions incorporated in the mass balance equations of the reactive species are expressed by the second order polynomial equations as a function of total polymerization time (T) in Table 3. Since the velocity profile of the reaction mass is expected to be highly dependent on the total reaction time (obtained from total volume of reactor/feed velocity), it is reasonable to relate the two using empirical relations given in the table. The best fit values of constants obtained for the three experimental cases are also given in the table. Even though the three data sets have different temperature profiles in the zones, the changes in values from one data set to another data set are insignificant in most cases. The equations given in the table can be used to predict the constants for an unknown set of reaction conditions.

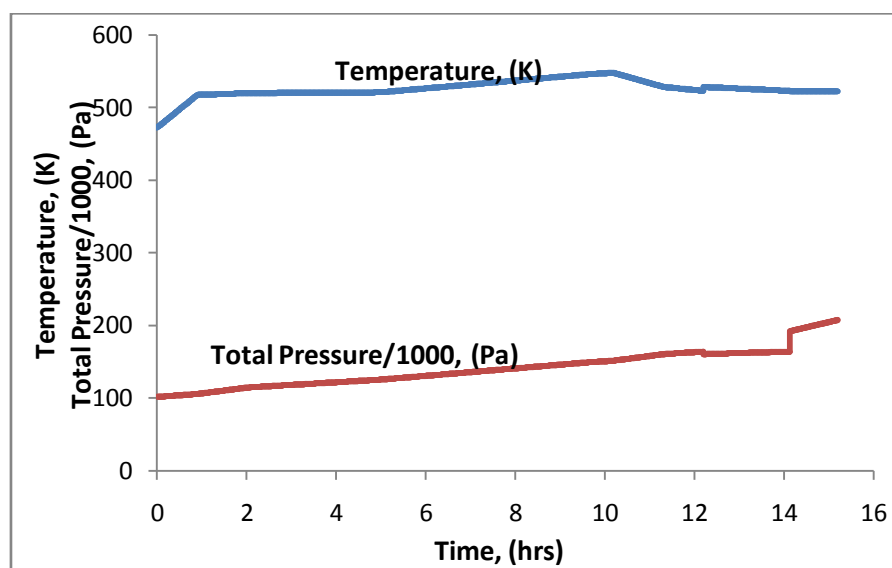


Figure 2: Graph of Polymer Mass Temperature (Measured) and Total Pressure (Predicted) Down the Length of VK Tube with Respect to Time for Data 3

c) Temperature and Pressure Estimation

Three sets of experimental data measured from a nylon-6 polymerization VK tube were used for the modelling and simulation of the process. At any point of time, the total pressure in the reactor was calculated by using water seal length above the reactor, the atmospheric pressure and the pressure exerted by the mass of polymer above the interested point in the reactor. The reactor design parameters were used to determine the time of the reactions and the hydrostatic pressures of the polymer mass at any point along the length of the reactor. The temperatures of the polymer mixture were measured at different points in the reactor. Straight line assumption has been used to interpolate

the temperature values between any two closely measured points. The temperatures and the properties of the polymer mixture have been listed in Table 3 in all the zones for three sets of experimental data

d) Starting parameters used in the simulation of the model

The modified mathematical model represented by the set of non-linear ordinary differential equations were solved simultaneously by using Runge- Kutta IV order method, with an iteration step size of 0.01h. To break the hierarchy of equations closure conditions²¹ were used. The starting parameters for all the three data sets were as follows:

$[m_0] = 8.837 \text{ mol/kg}$; $[P_1] = 0.0 \text{ mol/kg}$; $\lambda_0 = \lambda_1 = \lambda_2 = 0.0$; $[C_2] = 0.0 \text{ mol/kg}$; $\lambda_{0x} = \lambda_{1x} = \lambda_{2x} = [P_{1x}]$; Water fed = $[W] = 1.3889 \text{ mol/kg}$ of mass = 2.5 wt% of input caprolactam Starting value of temperature = 473 K (considered)

Table 4: Experimental Nylon-6 Polymerization Reactor Data Collected for Three Different Sets of Data

Property ^a	Data 1		Data 2		Data 3	
Reaction Time(H)	11.71		14.5		15.17	
Acetic Acid Fed, (Wt%) (Mol/Kg)	0.07 0.0117		0.07 0.0117		0.06 0.0100	
	Melt ^b Temp (K)	Dow ^c Temp (K)	Melt ^b Temp (K)	Dow ^c Temp (K)	Melt ^b Temp (K)	Dow ^c Temp (K)
T ₁ (Zone I)	517	-	518	-	521	-
T ₂ (Zone II)	521	546	520.5	538	521 550	
T ₃ (Zone III Upper)	524	555	522	549	527 550	
T ₄ (Zone III Lower)	548	555	546.5	549	547 550	
T ₅ (Zone IV)	531.5	497	529	501.5	531 504	
T ₆ (Zone V)	526.5	496	523.5	501.5	527 505	
Extractables(%)	10.56		9.62		9.66	
M _n (G/Mol)	17084		16.484		16.384	
[COOH](Mol/Kg)	0.0517		0.0548		0.0590	
[NH ₂](Mol/Kg)	0.0460		0.0452		0.0480	

^{a, b, c} as defined elsewhere²⁴

The properties of polymer such as number-average molecular weight (M_n), $[COOH]$, $[NH_2]$, polydispersity index (excluding the effect of caprolactam and cyclic dimers) and the quantity of extractables have been determined.

III. DATA FROM INDUSTRIAL OBSERVATIONS

The change in pressure down the length of the reactor and the temperature of the polymer mixture in various zones were measured by finding the average of 10-12 values, found after every two hours and are

presented in Table 4. The resident time of polymer mass in each zone was measured by using the mechanical dimensions and the internal structure of the tube. The polymer properties were measured from the polymer samples collected at the bottom of the reactor in the raw form before the monomer was extracted at every two hours. The relative viscosity was calculated by the methods given in literature²² and the average values were listed in Table 3. The following equations were used to find M_n , relative viscosity (RV_c) and extractables wt% (E) from the experimental raw chips and were

presented in Table 3. Intrinsic viscosity

$$[\eta] \text{ (dL/g)} = \{ [1 + 4K_H(RV_c - 1)]^{1/2} - 1 \} / 2K_H(1 - 0.01E) \quad (6)$$

Relative viscosity (extracted chips)

$$RV_1 = 1 + [\eta] + K_H[\eta]^2 \quad (7)$$

Number-average molecular weight

$$M_n \text{ (g/mol)} = 113.16F(RV_1 - 1) \quad (8)$$

where k_H is the Huggins constant (0.286 for nylon-6 polymer) and F is an empirical relation constant²³ determined for the industrial reactor (95.7). The refractive index was measured by an immersion refractometer. The percent of extractables can be measured by refluxing 15.0g of raw chips for 8 hours in 80ml of distilled water. The refractive indices calibration table was used for various concentrations of caprolactam to obtain the percentage of extractables.

IV. RESULTS AND DISCUSSION

a) Water concentration, temperature and total pressure calculation down the reactor

Total pressure and temperature along the length of the reactor were calculated using the procedure explained elsewhere²⁴. The pressure of the polymer melt varies from 1.023×10^5 Pa to 2.081×10^5 Pa down the length of the reactor. Moreover, the viscous polymer mixture flowing down the VK tube decreases the pressure. However these changes are very small to be neglected. The temperature at any point was measured by linearly interpolating the two measured points. The temperature and pressure profiles along the length of the system were plotted in Figure 2 for data 3. The volumes of the various portions and the mass flow rate into the VK tube were used to calculate the reaction times. The temperature and pressure values were shown with respect to the estimated polymerization time at all points from the top to the bottom of the reactor.

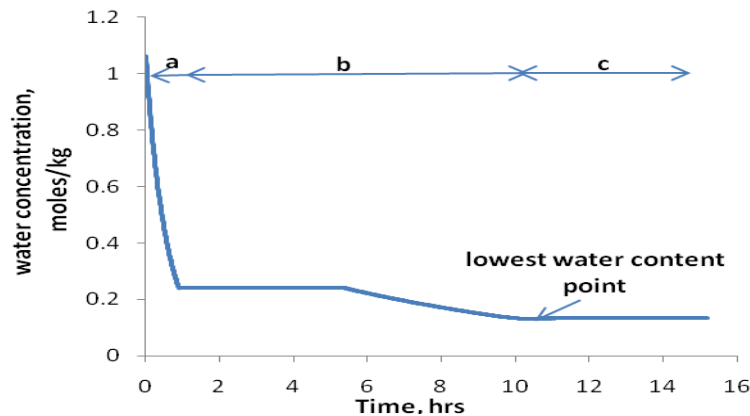


Figure 3: Water Profile Down the Length of the Vk Tube Versus Polymerization Time for Data 3: (A), (B), and (C) As Explained Elsewhere²⁴.

Table 5: Comparison Between Predicted Results of Polymer Properties with Experimental Values for the Three Data Sets

Property	$[\text{NH}_2]^b$ (mol/kg)	M_n^c (g/mol)	Extractable (%)	C_1 (wt%)	$C_1 + P_1 + C_2$ (wt%)	$[\text{COOH}]^b$ (mol/kg)
Actual – Industrial data	0.0460	17084				0.0517
Data I : Old model						
f=0.65	0.0466	16750		9.00	9.02	0.0542
f=0.75	0.0460	16564		8.99	9.01	0.0548
Error (%)	1.0	2.0	10.56	14.8	14.6	4.6
	0.0	3.0		14.9	14.7	6.0
Data I : Present Model						
f=0.65	0.0459	17356		9.34	9.35	0.0534
f=0.75	0.0453	17161		9.32	9.34	0.0541
Error (%)	0.2	1.6		11.6	11.5	3.2
	1.5	0.4		11.7	11.6	4.6

Actual – Industrial data	0.0452	16484				0.0548
Data II: Old Model						
$f=1.0$	0.0451	16096		8.41	8.43	0.0567
Error (%)	0.2	2.4	9.62	12.6	12.4	3.5
Data II : Present Model						
$f=1.0$	0.0448	16358		8.40	8.42	0.0564
Error (%)	0.8	0.8		12.7	12.5	2.9
Actual – Industrial data	0.0480	16384				0.0590
Data III : Old Model						
$f=0.8$	0.0467	16703		8.33	8.35	0.0547
Error (%)	2.7	1.9	9.66	13.8	13.6	7.2
Data III : Present Model						
$f=0.8$	0.0484	16379		8.19	8.21	0.0564
Error (%)	0.8	0.03		15.21	15.01	4.0

b) VK tube reactor model

The assumed constant flow profile of the feed to the top of the reactor and down the length of the VK

tube reactor as per our earlier work was modified in the present model to include the non linear time dependent factors (due to deviation from plug flow profile).

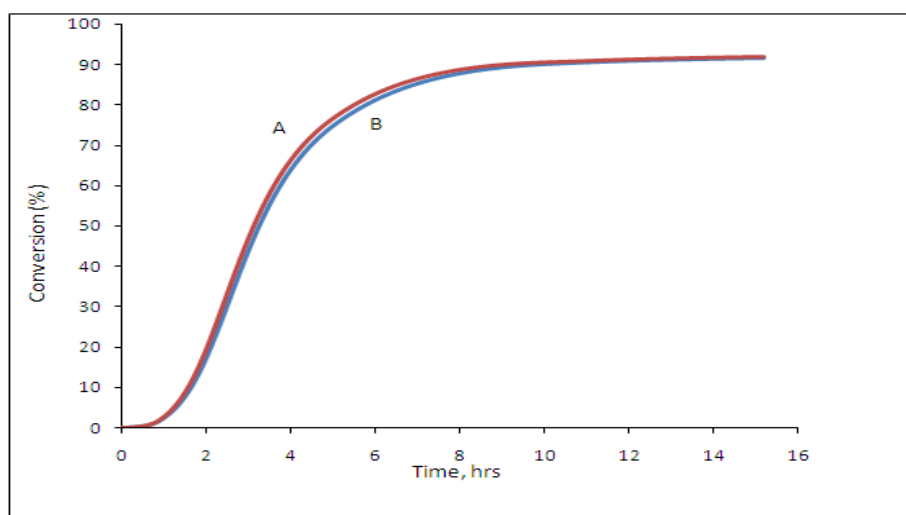


Figure 4: Predicted Conversions Comparison for Case 3: (A) Old Model, (B) Present Model

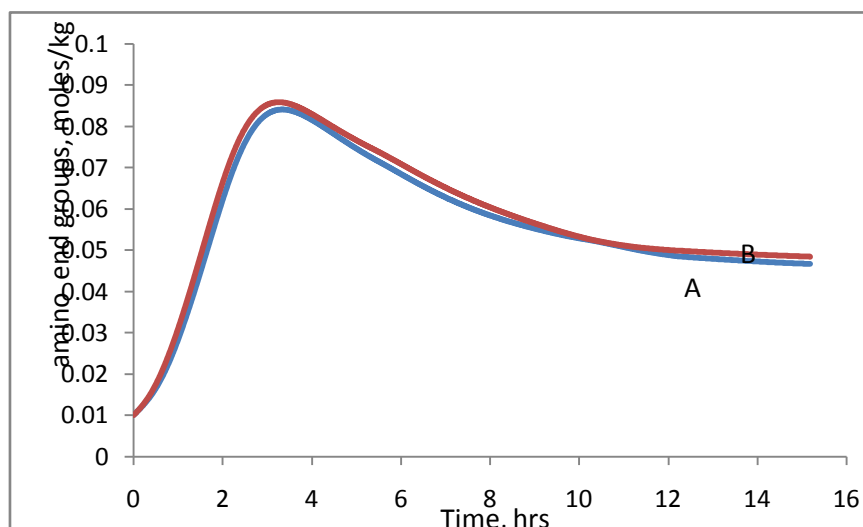


Figure 5: Predicted Amino end Groups Comparison for Case 3: (A) Old Model, (B) Present Model

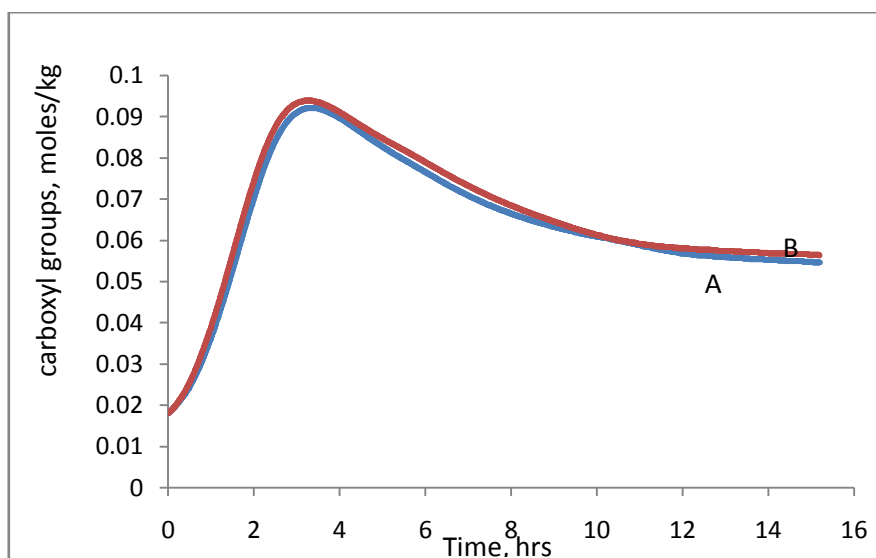


Figure 6: Predicted Carboxyl end Groups Comparison for Case 3: (A) Old Model and (B) Present Model

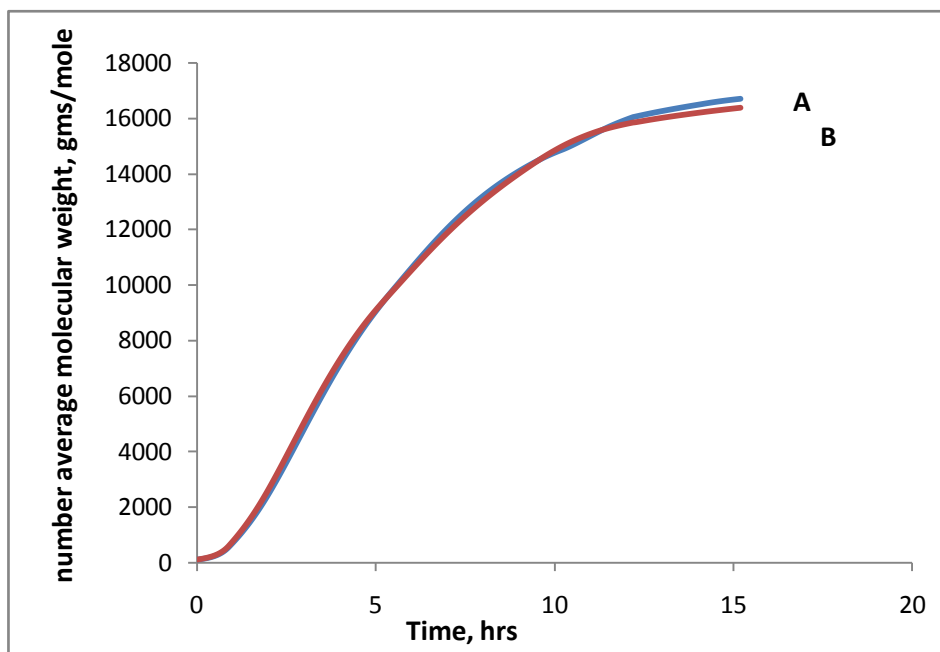


Figure 7: Predicted M_n Values Comparison for Case 3: (A) Old Model (B) Present Model

c) Comparison of predicted polymer properties with the experimental results.

The conversion of caprolactam plotted versus polymerization time (Figure 4) revealed increased faster conversion in the first 3-8 hours and attained equilibrium thereafter. The rates of the conversion in the present model are slower than in the previous model because of the slightly controlled vaporization of water in the top zone of the reactor. The present model determined a monomer (m) concentration of approximately 8.2 % when polymerization was completed. The result has been compared with the experimental extractables concentration of 9.66% in Table 3. The difference is

about 14%. For the other two data sets also similar results were obtained. The estimation was not so good because the experimental extractables contained around 15-20 wt% of cyclic and linear oligomers along with the remaining monomer (m).

d) Similar results were obtained in the earlier model²⁴ as well.

This is because both the models are not capable of calculating the concentrations of higher oligomers and hence a better comparison could not be made. Figures 5-7 depict the comparison between the predicted values for $[NH_2]$ end groups, $[COOH]$ end

groups and number average molecular weight for old model²⁴ and present model. The comparison has also been presented in Table 3. In the present model, the end group concentrations increase in the middle zone and in the bottom zone of the reactor better than the old model because of more water retained due to the controlled vaporization by the induced velocity. However in the bottom zone M_n values decrease in the present model because of the increased quantity of water due to the controlled vaporization in the top and the middle zones. This happens because of the assumed non plug velocity profile where water moves down the reactor at a faster rate than when there is flat velocity profile for the flow of the reactants. The error percentages reduced considerably for the carboxylic end groups and the M_n values. The predicted values for the present model incorporating the non-linear time dependent effect for the various species namely, caprolactam, polymer,

water and acetic acid gives the better comparison for carboxylic end groups and M_n values with the experimental values. The errors in amino end groups were also improved considerably in some cases. The improved results are due to adjustment of concentrations of various species induced due to non-flat velocity profile, which controls the reaction rates of the polymerization process in the top zone and in the

middle zone thereby maintaining the required quantity of water concentration for better results. This helps to control the end polymer properties and the M_n value of the end polymer.

e) *Validation of the present model in predicting the effects of pressure and temperature down the VK tube reactor*

In Figure 8, the influence of head pressure, that is the pressure caused by the water seal at the top of the reactor can also be observed to affect the M_n value of polymer. For instance, when the water seal length is increased from 0.1 - 5m, rates of reactions improve significantly because of the retention of huge quantity of water inside the reactor. However M_n decreases by about 10.7 % (Figure 8) because of the higher quantity of water at equilibrium. Similar results were obtained in the old model²⁴. As discussed in the previous section, down pressure in the reactor was observed to be a controlling parameter. This is observed from Figures 9-12 as the discrepancies between the experimental values and the predicted model values were significant. Therefore, the reaction rates and the end product values at the bottom of the reactor can be controlled using the pressure in the reactor.

f) *Similar performance was obtained using the earlier model²⁴ as well*

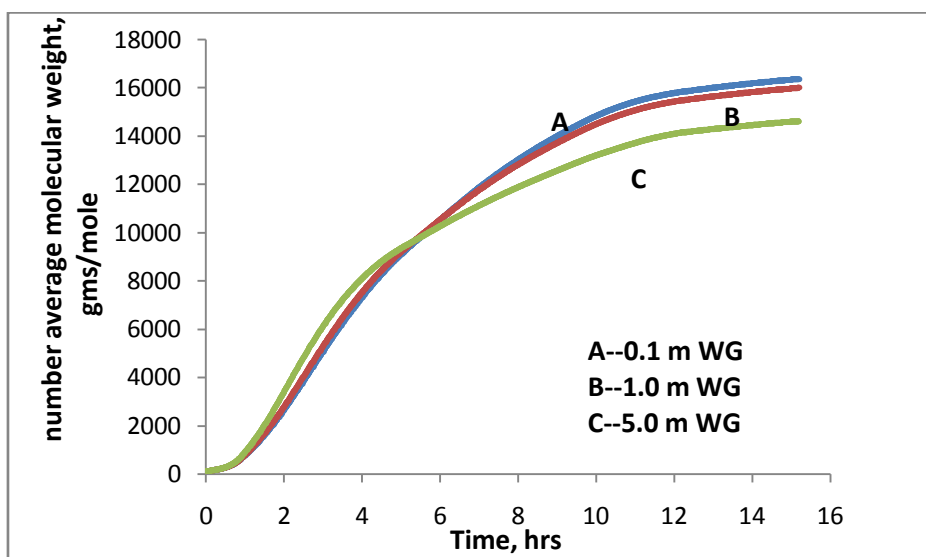


Figure 8: Influence of Water Seal Length on M_n for Data 3

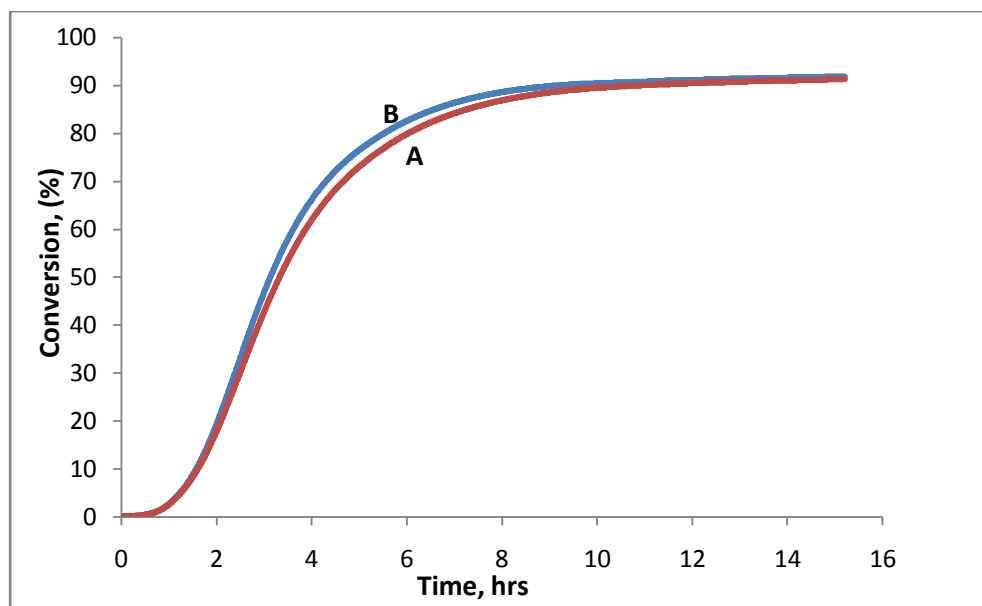


Figure 9: Predicted Conversions Comparison for Data 3 With the Present Model: (A) With Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal at mospheric Pressure

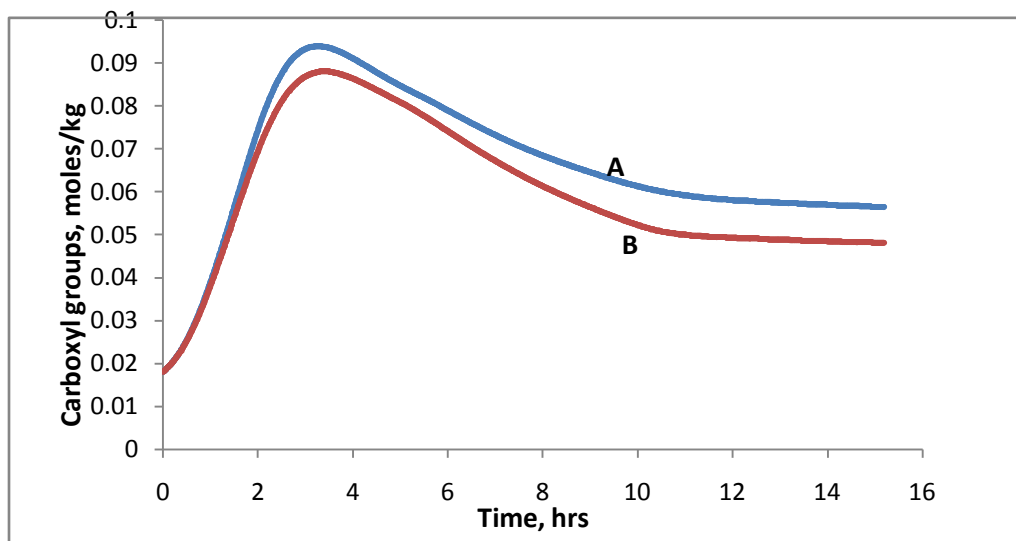


Figure 10: Predicted [Cooh] Concentrations Comparison for Data 3 Using the Present Model: (A) with Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal At mospheric Pressure

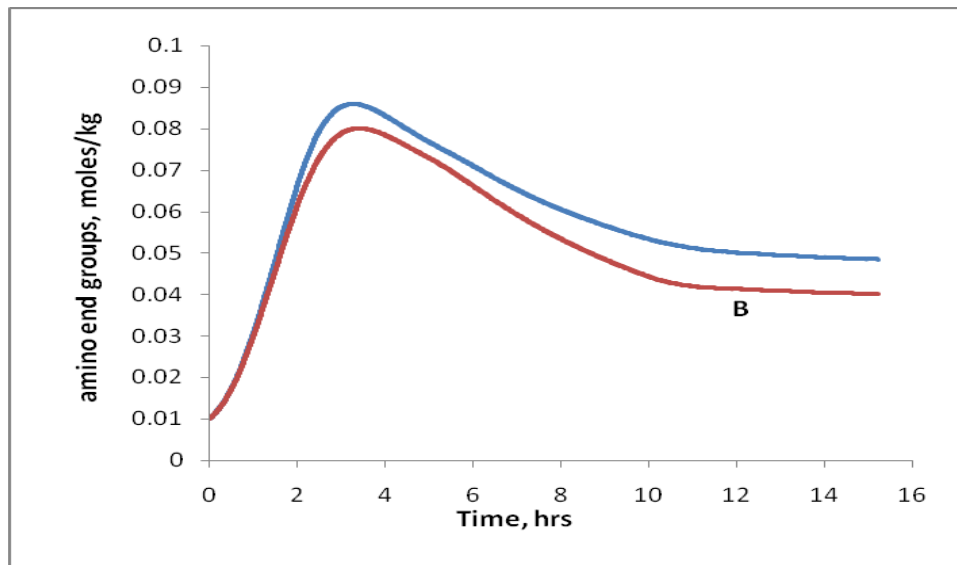


Figure 11: Predicted $[NH_2]$ Concentrations Comparison for Data 3 Using the Present Model: (A) with Hydrostatic Pressure Variation in the Vk Tube and (B) At Normal Atmospheric Pressure

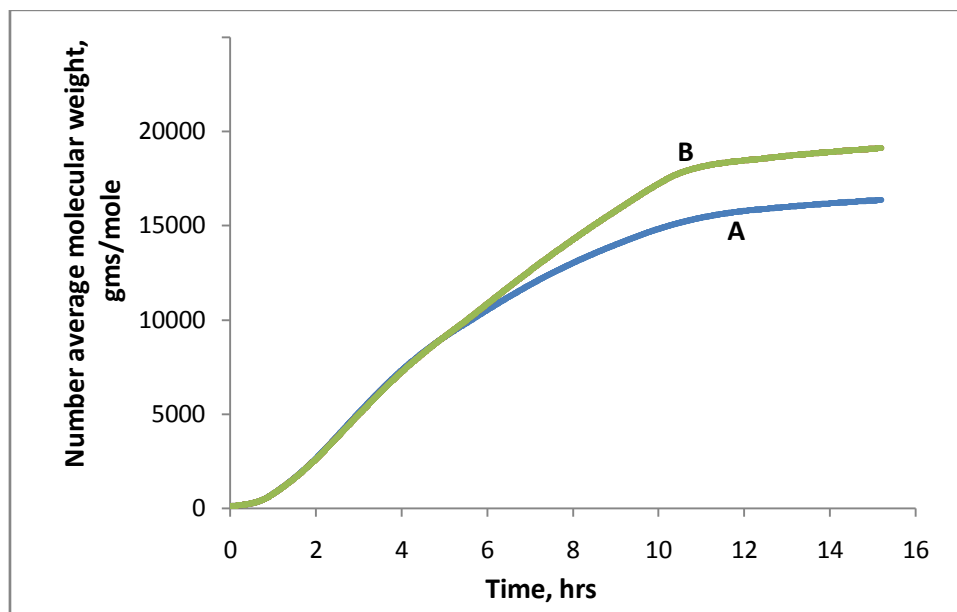


Figure 12: predicted m_n values comparison for data 3 using the present model: (a) with hydrostatic pressure variation in the vk tube and (b) at normal atmospheric pressure

VK tube reactor's performance can be optimized by another important parameter, the polymer melt temperature profile down the reactor. To get the proper initiation of the reactions water should be retained at the beginning by slowly increasing the temperature to the highest temperature point. Thereafter, water should be allowed to evaporate to the required quantity at the maximum temperature and then reduced to the expected equilibrium value. The properties of the polymer at the end of the reaction are

determined by the water content at the highest temperature point. If the highest temperature point is increased there will be a decrease in $[W]$ in the non-vaporizing zone. This will increase the average molecular weight as shown in Figure 13. Therefore, the temperature at the maximum temperature position (T_h) affects the final polymer properties. When the maximum temperature (T_h) has been changed nominally by a few degrees (10K), M_n changes by about 21.6%. Similar behaviour was observed in the previous model²⁴.

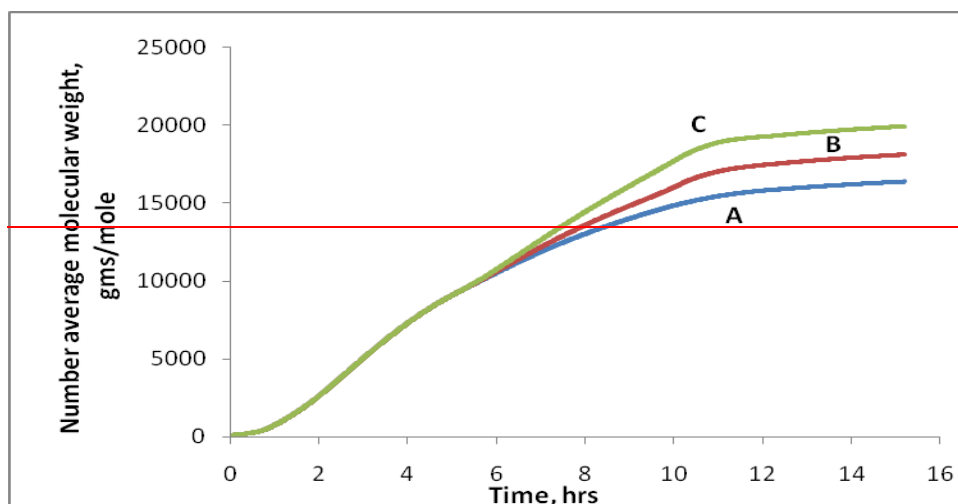


Figure 13: Highest Temperature (T_h) Influence on M_n For Data 3:
A-548 K, B-558 K, C-568 K

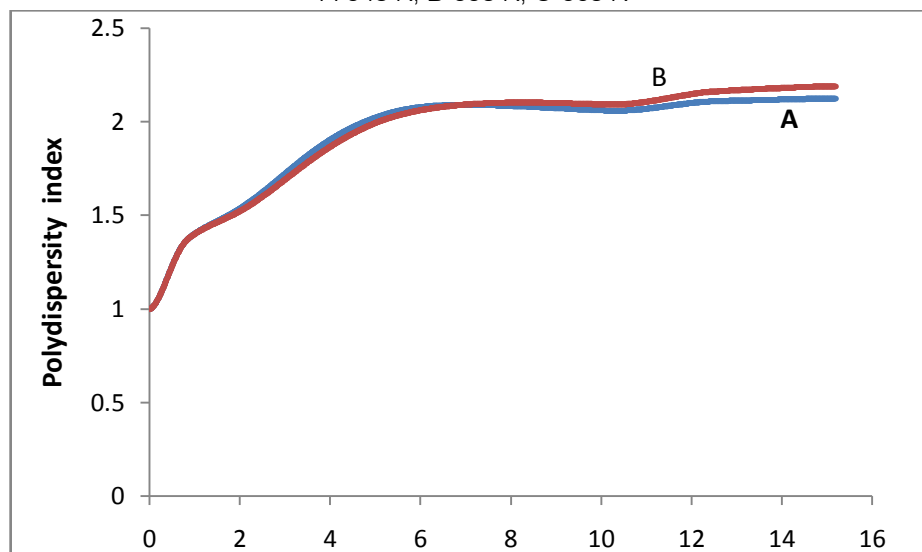


Figure 14: Predicted Polydispersity Index Values Comparison For Data 3: (A) With The Influence Of Pressure Variation In The Vk Tube And (B) At Normal Atmospheric Pressure

Table 5: Listed Polydispersity Index Values With Respect To Polymerization Time For Data 3

Time(H)	M_w/M_n
0.0	1.0003
1.0	1.4014
2.0	1.5364
3.0	1.7220
4.0	1.9035
5.0	2.0215
6.0	2.0782
7.0	2.0907
8.0	2.0851
9.0	2.0735
10.0	2.0615
11.0	2.0696
12.0	2.1002
13.0	2.1130
14.0	2.1192
15.0	2.1232

The predicted net reaction values and the equilibrium values of the three major reactions have

V. CONCLUSIONS

Following conclusions could be drawn from the present work:

- The Nylon-6 polymerization was simulated in an industrial VK tube reactor using a modified non-linear model incorporating a time dependent modification function, T.
- Non-linear time dependent decay functions were introduced in mass balance equations for calculating the concentrations of various species at any position in the reactor to account for the change in concentration of the species due to non-flat velocity profile. This reduces the errors compared to models that use a strict plug flow model for a VK Tube. Since the internal design of the VK Tube is not ideally suited to achieve a flat velocity profile, the incorporated functions tries to accommodate small differences from the ideal condition of plug flow.
- A modified empirical VLE relation was used in the vaporizing zone to predict the water profile inside the reactor incorporating the non-linear time dependent functions as mentioned above.
- A lowest water content (LWC) point was noted, which defined the end of the vaporizing zone, due to the changing temperature and pressure down the axis of the reactor. The location and $[H_2O]$ at the LWC point were observed to be very important in determining the end product results.
- The non-flat velocity profiles of the various reactants in the VK tube reactor controlled the reaction rates, controlled the vaporization of water to the required Quantity in the vaporizing zone and in the non-vaporizing zone that favoured simulation of polymer properties with exceptional accuracy.
- The calculated values of M_n for data 3 by the present model evaluates the industrial data with an error of 0.03, as compared to the previous model with an error of 1.9%.
- Amino end group concentrations were predicted by the present model for data 3 with an error of 0.8% as against the prediction error of 2.7% in the earlier model.
- Carboxyl end groups predicted by the present model for data 3 match with the industrial data with an error of 4% over the error of 7.2% in the previous model.
- The present model was found to be in conformity with the experimental values, superior over the earlier model²⁴, where the reactants were assumed to flow in a perfect flat velocity profile.

been depicted in Figures 15 and 16. The pattern and the performance are similar to those of earlier model ²⁴

- Hence it can be concluded that the present non-linear explicit time dependent simulation model is useful in estimating the nylon-6 end group results in a VK tube reactor accurately, in improving the system operation and provides insights for the improvement of such reactor designs.

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