Modelling of VK column reactors for manufacturing nylon-6

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A stagewise model based on tanks in series approach has been proposed to elucidate the effects of backmixing in the two-phase zone of VK (Vereinfacht Kontinuerlich) column reactors. A recycle stream between tanks has been used to represent backmixing due to the vapour stream rising countercurrently to the liquid stream. The model has been used to calculate the monomer conversion, number average degree of polymerization and the polydispersity index at the end of the reactor. It has been found that increased backmixing increases the water holding capacity of the stream and, therefore, increases the conversion at the end of the two-phase zone. As water also lowers the degree of polymerization, it has been found that at the end of the reactor where equilibrium is reached, the degree of polymerization decreases with increased backmixing in the top portion of the reactor. The polydispersity index remains relatively unaffected as equilibrium is attained at the end of the reactor. If too high temperatures are used at the beginning of the reactor, the streams would contain less water and this would lead to higher degrees of polymerization but to lower rates.

Keywords: Backmixing, Nylon-6, Polymerization, Vertical column reactor

1 Introduction

Hydrolytic polymerization of e-caprolactam consists of polymerizing caprolactam in the presence of water and is carried out either batchwise or continuously. Sittig\(^1\) has summarized the various reactor arrangements such as batch reactors operating under high pressure, cascades of stirred tank reactors, tubular reactors, etc. The present work focuses on one type of continuous tubular reactor—the VK column. A sketch of the reactor is given in Fig. 1. It consists of two zones. The top zone of the reactor is a two-phase gas-liquid bubble column reactor while the bottom zone is a single-phase tubular reactor. Usually, the bottom zone is modelled as a plug flow reactor (PFR). The mass fraction of vapour phase in the top reactor, or the quality of the mixture in the two-phase flow terminology, is high and hence the countercurrent flow of the vapour causes vigorous mixing action. In view of this, it has been customary to model the phase part of the reactor as a single continuous stirred tank reactor (CSTR). In such a scheme, the entire VK column is modelled as a CSTR followed by a PFR. Jacobs and Schweigman\(^2\) and Naudin ten Cate\(^3\) utilized such models to analyze VK column reactors.

A rough estimate made from the data available in the open literature indicates that the residence time in the two-phase zone could be as much as 30% of the total residence time. Further, as the quality of the mixture decreases with depth in the two-phase zone, the mixing action of the vapour would be less vigorous there. In other words, the reaction mixture throughout the two-phase zone might not be homogeneously mixed. In view of

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**Fig. 1—VK column**
both these factors, the approximation of the entire two-phase zone by a single CSTR is open to criticism. Moreover, as the reaction is carried out essentially to equilibrium in VK column, the water content of the reaction mixture at the end of the two-phase zone essentially determines the nature and properties of the product at the end of the single-phase zone as well. Thus, it is desirable to have a more realistic model of the two-phase zone of the reactor. Gupta and Gandhi proposed a model with stagewise backmixing. Tai and Tagawa did extensive work on the kinetics of nylon-6 polymerization. Gupta et al. also followed Tai's kinetic scheme in their model of industrial reactors. Using their kinetic scheme, detailed predictions of the proposed model have been made and are reported in this paper.

2 Model for the Reactor
2.1 Reaction Mechanism and Kinetics

The hydrolytic polymerization is known to consist of five reversible reactions:

(i) Ring opening

\[ \text{HN(C}_{2}\text{H}_{5}	ext{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \rightarrow \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \]

(ii) Polyaddition

\[ \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \rightarrow \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \]

(iii) Polycondensation

\[ \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \rightarrow \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \]

(iv) Polyaddition of cyclic dimer

\[ \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \rightarrow \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \]

(v) Ring opening of cyclic dimer

\[ \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \rightarrow \text{HN(C}_{2}\text{H}_{5}\text{)}\text{C}=\text{O} + \text{H}_{2}\text{O} \]

The rate expressions, derived earlier by Gupta and Gandhi are summarized in Appendix 1. These equations are different from those given by Tirrell et al. but are consistent with those given by Hermans et al., Hoftpizer et al. and Reimischueskel. The reaction rate constants for reactions are usually represented as follows:

\[ k_i = k^{\circ}_i + k^*_i C; \quad (i = 1-5) \]

where \( k \) is the reaction rate constant; \( C \), the concentration of acid end group in mol/kg; and superscripts \( u \) and \( c \) refer to catalysed and uncatalysed parts.

The above representation reflects the fact that all the reactions are catalyzed by carboxyl end groups. The rate and equilibrium constants are temperature dependent and an Arrhenius type relationship can be used:

\[ k_j = A_j \exp (-E_j / RT); \quad j = u \text{ or } c \]

where \( A \) is the frequency factor; \( E \), the activation energy; \( R \), the gas constant; and \( T \), the temperature in K.

The above representation reflects the fact that all the reactions are catalyzed by carboxyl end groups. The rate and equilibrium constants are temperature dependent and an Arrhenius type relationship can be used:

\[ K_j = \exp \left[ -\left( H_j - T S_j \right) / RT \right] \]

where \( H \) is the enthalpy; and \( S \), the entropy.

The values given by Arai et al. have been used and are listed in Table 1.

2.2 Model with Stagewise Backmixing

The most important feature of the top portion of the reactor is the backmixing caused by the bubbling action of the vapour phase. The effect of mixing in two-phase bubble columns has been evaluated on the basis of axial dispersion models as well as by stagewise models such as tanks-in-series models, etc. In view of the computational

<table>
<thead>
<tr>
<th>( i )</th>
<th>( j )</th>
<th>( A_i ) (cal/mol)</th>
<th>( E_i ) (cal/mol)</th>
<th>( H_i ) (cal/mol)</th>
<th>( S_i ) (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( u )</td>
<td>( 5.9874 \times 10^5 )</td>
<td>( 1.988 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
<tr>
<td>2</td>
<td>( c )</td>
<td>( 4.3075 \times 10^7 )</td>
<td>( 1.8806 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
<tr>
<td>3</td>
<td>( u )</td>
<td>( 1.8942 \times 10^{10} )</td>
<td>( 2.3271 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
<tr>
<td>4</td>
<td>( c )</td>
<td>( 1.2114 \times 10^9 )</td>
<td>( 2.067 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
<tr>
<td>5</td>
<td>( u )</td>
<td>( 2.8558 \times 10^9 )</td>
<td>( 2.2845 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
<tr>
<td>6</td>
<td>( c )</td>
<td>( 1.6377 \times 10^9 )</td>
<td>( 2.2845 \times 10^4 )</td>
<td>( 1918 )</td>
<td>( -78846 )</td>
</tr>
</tbody>
</table>
simplicity as well as the objective of quantitative but comparative exploration of mixing effects, a stagewise model was proposed earlier by Gupta and Gandhiv for this purpose. Selection of stagewise model is also partly justified by the presence of baffles and heating sections in the reactor. The model consists of three tanks in series with a recycle liquid stream in between. The recycle stream represents the backmixing caused by the upward moving vapour bubbles. A figurative depiction of the model is shown in Fig. 2. Models such as these have been used earlier by Mecklenburgh and Hartland, and Chianese et al. The number of tanks has been selected to be three, guided partly by the fact that some industrial reactors contained three subzones in the top portion and partly by the equivalences between the axial dispersion and the tanks-in-series models for the second order reaction presented by Levenspiel.

Mecklenburgh and Hartland presented a criterion for correspondence between axial dispersion and mixing models and the magnitude of the fraction of the recycle stream \( \alpha \) has been varied between 0 and 1. These choices have been justified earlier.

The three CSTRs shown in Fig. 2 are connected by the vapour streams emerging from the tanks below. Thus, the first and second tanks receive a vapour stream from the second and third tanks respectively. The vapour stream leaving the first tank is sent to a condenser and the caprolactam is recycled to the top of the reactor. The third tank, however, will not receive a vapour stream as the portion below it is a single-phase reactor. The three tanks have been assumed to be at different temperatures. Thermal equilibrium has been assumed via the well-stirred nature of the tanks. The residence time in each of the tanks has been assumed to be one hour, giving a total residence time of three hours in the two-phase region. It is approximately 30% of the total residence time in a typical VK column. The feed rate has been arbitrarily selected as 1000 kg/h, a typical production figure. Jacobs and Schweigman reported thermodynamic equilibrium to exist between the liquid and gas phases as far as mass transport is concerned. Earlier estimates of mass transfer coefficients supported this. It was, therefore, assumed that the vapour and liquid phases would be in local thermodynamic equilibrium throughout the two-phase zone of the column.

### 2.3 Mathematical Description of the Model

The equations describing the polymerization processes in the model described are given below.

The mass balances for monomer, water, aminocaproic acid and n-mers in the first tank respectively are:

\[
\begin{align*}
F_0 M_0 - F_0 M_1 + aF_0 M_2 - aF_1 M_1 + G_1 M_2' + \rho V_1 r_m &= 0 \\
F_0 W_0 - F_0 W_1 + aF_0 W_2 - aF_1 W_1 + G_1 W_2' + \rho V_1 r_w &= 0 \\
-F_1 s_{1,1} - aF_1 s_{1,2} - aF_1 s_{1,1} + \rho V_1 r_{s_{1,1}} &= 0 \\
-F_1 C_{d,1} + aF_1 C_{d,2} - aF_1 C_{d,1} + \rho V_1 r_{c_{d,1}} &= 0 \\
-F_1 s_{n,1} + aF_1 s_{n,2} - aF_1 s_{n,1} + \rho V_1 r_{s_{n,1}} &= 0
\end{align*}
\]

where \( F \) is the liquid feed rate in kg/h; \( M \) and \( M' \), the concentrations of caprolactam (mol/kg) in liquid and gas phases respectively; \( G \), the vapour flow rate (kg/h) in two-phase zone; \( r \), the rate of formation of the respective quantities indicated by the subscript; \( V \), the volume of CSTR in m³; \( W \) and \( W' \), the concentrations of water (mol/kg) in liquid and gas phases respectively; \( s_{m} \), the concentration (mol/kg) of linear n-mer, \( H_2HN(CH_2)_n - C_6H_5OH \); \( s_{1} \), the concentration

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*The subscripts 1, 2, 3 on \( A, E, H, S, k \) and \( K \) refer to the reaction number and subscripts 0, 1, 2, 3 on all quantities other than above refer to the conditions in the space above the top of the reactor, in the first CSTR, in the second CSTR and in the third CSTR respectively.*
(mol/kg) of aminocaproic acid; \(\alpha\), the parameter characterizing the degree of backmixing; \(\rho\), the density of reaction mixture in kg/m\(^3\); and \(C_0\), the cyclic dimer.

In view of the units being used, i.e. mol/kg, the overall mass balance has to be written separately and is given by:

\[ F_0 - F_1 + G_1 - 0.018 W_1 G_0 = 0 \]  

(14)

and the gas phase compositions have to satisfy

\[ 0.113 M_1' + 0.018 W_1' = 1 \]  

(15)

The vapour liquid equilibrium relations for 1st tank give:

\[ W_1'(P_m + \rho gh) / (W_1' + M_1') = W_1 P_m / M_0 \]  

(16)

\[ M_1'(P_m + \rho gh) / (W_1' + M_1') = M_1 P_m / M_0 \]  

(17)

where \(P_m\) is the pressure above melt (1 atm); \(g\), the acceleration due to gravity; \(h\), the height of CSTR's taken to be 1.2m; and \(P^{\text{w}}_m\) and \(P^{\text{d}}_m\) are the vapour pressure (atm) of water and caprolactum respectively.

Similarly, the modelling equations for other tanks can also be written. In the above equation, \(\rho V_t = \tau F_t\), where \(\tau\) is the residence time in the CSTR.

Generally, three properties of the product are of interest: conversion, number average degree of polymerization (DP) and the polydispersity index (PDI) which is the ratio of the weight average degree of polymerization and DP. Noting that

\[ C = \sum_{n=1}^{\infty} s_n u_0 \text{ and } Z + C = \sum_{n=1}^{\infty} n s_n = u_1 \]

(where \(Z\) is the concentration of amide group in mol/kg), it is observed that \(\text{DP} = (Z + C) / C\) can be easily calculated if the zeroth and first moments of the molecular weight distribution (\(u_0\) & \(u_1\)) represented by \(s_n\) are evaluated. The second moment of the distribution (\(u_2\)), defined as

\[ u_2 = \sum_{n=1}^{\infty} n^2 s_n \]

has to be evaluated to get PDI, since PDI = \(u_0 u_2 / u_1^2\).

2.3.1 Calculation of Conversion and DP

Equation for \(C\) can be obtained for the first tank by summing Eqs (11) and (12) for \(n \geq 2\). Similarly, an equation for \(Z + C\) can be obtained by multiplying Eq. (12) by \(n\) and summing for \(n \geq 2\) and adding the sum of Eq. (15). The resulting equations are:

\[ -F_1 C_1 + \alpha F_1 C_2 - \alpha F_1 C_1 + \rho V_1 r_{c_1} = 0 \]  

(18)

\[ -F_1 C_1 + \alpha F_1 C_2 - \alpha F_1 C_1 + \rho V_1 (r_{c_1} + r_{c_2}) = 0 \]  

(19)

A total of thirty nonlinear algebraic equations, ten for each tank, have to be solved simultaneously to obtain conversion and DP. As an example, Eqs (9) to (19) are the equations for the first tank. One more assumption is required to do this as \(r_1\) involves \(s_2\). It is well known that assuming \(s_2 = s_1\) or estimating \(s_2\) by Flory's distribution gives the results differing only insignificantly. Here, it was assumed that \(s_2 = s_1\).

A form of Raoult's law, suggested by Jacobs and Schweigman\(^2\) on the basis of their data, has been used to calculate the vapour-liquid equilibrium relations. This is exemplified in Eqs (16) and (17). Tai and Tagawa\(^6\) quoted the data of Fuku- moto on vapour-liquid equilibria of caprolactam-water-nylon\(^6\) system. However, these data are applicable for caprolactam concentrations of less than 13 wt % or at high conversions. Our attempts to fit the data of Giori and Hayes\(^{19}\) in a form suitable for the present work were unsuccessful. In view of all this, it was decided to stick to the above mentioned Raoult's law type of formulation. The vapour pressure of water was calculated from the correlation given by Sherwood et al:\(^{20}\):

\[ \ln P^{\text{w}}_m \text{ (in atm)} = 11.6703 - \frac{3814.44}{T(K)} - 46.13 \]  

(20)

It might be mentioned here that Eq. (20) is very different from that given by Tai and Tagawa\(^6\). We used Eq. (20) as the equation given by Tai and Tagawa did not fit the observed vapour pressures of water and gave large deviations starting from 100°C onwards. The vapour pressure data for caprolactam given by Snell and Ettre\(^{21}\) has been fitted to Clausius-Clapeyron's equation and was used in the following form:

\[ \ln P^{\text{w}}_m \text{ (in atm)} = 13.006 - \frac{7024.023}{T(K)} \]  

(21)

The reaction mixture from the third tank flows to the PFR where boiling does not occur. The equations that describe a PFR are identical to those of a batch reactor which have been summarized in Appendix 1. The PFR calculations were done at the same temperature as that of the last tank. It is clear that the outlet conditions of the third tank form the inlet conditions of PFR.

2.3.2 Calculation of PDI

The equations for the first three moments were solved using a closer approximation for the fourth moment based on Laguerre polynomials given by
The equation for the $r$th moment of the $s_n$ distribution in the first tank is obtained by multiplying Eq. (12) by $n^r$ and summing it from $n=2$ to $\infty$ and adding Eq. (11) to the sum. The equations for the second and third tank can be similarly obtained. These are given by:

$$-F_{u_1} + \alpha F_{u_2} - \alpha F_{u_3} + \rho V_r u_1 = 0 \quad \ldots (22)$$

$$-F_{u_1} + \alpha F_{u_2} - \alpha F_{u_3} - F_{u_2} - \alpha F_{u_3} = 0 \quad \ldots (23)$$

$$-F_{u_1} + \alpha F_{u_2} - \alpha F_{u_3} - F_{u_2} - \alpha F_{u_3} + \rho V_r u_1 = 0 \quad \ldots (24)$$

where $u_r$ is the $r$th moment of $s_n$ distribution and

$$R_{u_1} = k_1 (W_t - S_{i,j}) + k_1 \sum_{i=1}^{r-1} \left( \frac{r}{x} \right) u_{r-1} u_{i,j}$$

$$- \frac{k_2}{k_2} \frac{W}{r+1} (S_{i} - u_{r+1}) + \sum_{i=1}^{r^2/2} \frac{1}{r+1} (S_{i} - u_{r+1})$$

$$\times (-1)^{r-1} \left( \frac{r}{2l+1} \right) - B_i (u_{r-2} - S_{i,j}) + k_1 M \sum_{i=1}^{r} \left( \frac{r}{x} \right) u_{r-1}$$

$$+ \frac{k_3}{k_3} \left[ \frac{r}{2l+1} \right] u_{r-1} + S_{i,j} \right] \times i = 2,3$$

$$i = 1,2,3$$

where $B_1$ is the Bernoulli numbers as defined by Jolley.

The second moment $u_2$ in each tank can be obtained by solving the above equations for $r=2$ and 3 simultaneously using the closer approximation for $u_4$ as already mentioned. The equations corresponding to PFR are given by:

$$\frac{du_r}{dt} = u_r, \quad r = 2 \text{ and } 3 \quad \ldots (25)$$

The second moment of the molecular weight distribution at the end of PFR can be obtained by integrating Eq. (25) for $r=2$ and 3 by using the exit conditions of the third tank as the initial conditions for the PFR.

2.4 Numerical Computation Procedure

The modelling equations are highly non-linear algebraic equations. Good initial guesses are required for successful solution of these equations. Brown’s method was used for solving the equations. Runge-Kutta-Gill’s method as given by Ralston and Wilf was used for integrating the differential equations.

3 Results and Discussion

The modelling equations were solved to obtain the conversion of the monomer, the number average degree of polymerization, DP and the polydispersity index (PDI). In all calculations, the feed was assumed to contain 0.05 mol of water per mol of caprolactam.

A few calculations were done with a model containing only two tanks. The results cannot be directly compared as the temperatures of the tanks cannot be matched. However, the results obtained were qualitatively similar to those obtained for three-tank model and here we present the latter results.

As the three tanks would be at different temperatures, three sets of temperatures were selected which were in the range of temperatures indicated by Kwatra. For a set of temperatures selected it is not necessary that vapour phase would be generated in all the three tanks. The water content and the temperature would dictate the presence or absence of two phases. To establish the correct set of conditions, the following procedure was used. Calculations were made first by assuming that all three tanks would contain only liquid phase. The boiling points of the resulting compositions in all the three tanks were computed. If any of the boiling points was less than the temperature specified for that tank, then the solution obtained was clearly unphysical and rejected. This procedure rules out the possibility of all three tanks containing only liquid phase for all the temperature sets selected. Similar procedure also eliminated the possibility of only the first tank containing two phases for all the cases considered. The procedure was then extended to the case where two phases exist in all the three tanks to eliminate unrealistic solutions. Another check on the validity of the solutions was that all the vapour flow rates should be positive. It must be noted that when vapour phase is not generated in the last tank, there would be no vapour stream to or from the tank and correspondingly the recycle liquid stream flow rate would be zero. With all the cross checks, the solutions to these equations were established.

The results obtained for the two-phase zone are shown in Tables 2-4. The results for the entire reactor, i.e. up to the end of PFR, are shown in Figs 3-11. In these figures, the results for the two-phase zone are indicated by points located at 3 h residence time and those for the PFR by lines.

3.1 Effect of Backmixing

Tables 2-4 show the effect of backmixing on the two-phase zone performance. The parameter $\alpha$, which is the fraction of the liquid stream being recycled, is proportional to the extent of backmixing. The first column gives the two values of $\alpha$ which were used to make the calculations. The
two values given for $\alpha$ are the fractions of the recycle stream between the first and second zones and second and third zones respectively. The flow rate of the vapour stream coming out of the last tank would be less compared to that for the other tanks. Due to this, it is not necessary that the extent of backmixing be the same in all tanks. To reflect this effect, calculations were also performed with two different values of $\alpha$ for the two recycle streams. These are shown in Tables 2 and 3.

Now looking at the results given in Table 2 for 230-240-253°C, it is apparent that as $\alpha$ increases or as backmixing increases, the conversion in-
### Table 4—Two-phase results (250-260-270°C)

<table>
<thead>
<tr>
<th>Degree of backmixing α</th>
<th>Tank No.</th>
<th>Vapour phase leaving the tank</th>
<th>Liquid phase leaving the tank</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Flow rate kg/h</td>
<td>Mol. fr. of H₂O</td>
</tr>
<tr>
<td>0.0</td>
<td>1</td>
<td>68.34</td>
<td>0.406</td>
</tr>
<tr>
<td>0.0</td>
<td>2</td>
<td>9.82</td>
<td>0.314</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>59.11</td>
<td>0.428</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>7.29</td>
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<tr>
<td>1.0</td>
<td>1</td>
<td>50.01</td>
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</tr>
<tr>
<td>1.0</td>
<td>2</td>
<td>6.28</td>
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<tr>
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</tr>
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<td>0.5</td>
<td>2</td>
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<td>0.328</td>
</tr>
<tr>
<td>0.0</td>
<td>3</td>
<td>2.54</td>
<td>0.278</td>
</tr>
</tbody>
</table>

Increased conversion implies an increased value of DP as the amount of water consumed by reactions has been found to be approximately the same in all the cases. Thus, as the backmixing increases, the DP also increases, as shown in Table 2. Further, backmixing implies more heterogeneity in the molecular weight distribution. Thus, the polydispersity index should increase with increased backmixing. This is confirmed from the data given in Table 2.

Fig. 3 shows the results of monomer conversion as a function of residence time for the entire reactor. The PFR results are different for different cases only because the inputs to it are different. The output from the last tank has more water and less monomer content for larger values of α. This continues to be so as the mixture passes through the PFR as well. However, as water content has only a minor effect on the equilibrium conversion, essentially 90% conversion is reached in all the cases. Fig. 4 shows the results for DP as a function of residence time for the whole reactor. Streams with lower water content will polymerize to a higher value of DP at equilibrium since polycondensation occurs to a greater extent. Thus, more backmixing will lead to a lower DP. This is illustrated in Fig. 4 where DP reached continuously decreases as α is increased. In other words, the trend at the end of the two-phase zone is exactly reversed at the end of the PFR. It can be seen from Fig. 4 that the effect of backmixing in...
the top portion of the reactor on the final product properties is quite significant. Fig. 5 shows the values of PDI for the entire reactor as a function of the residence time. As the conversion reaches equilibrium values and as polycondensation occurs to greater and greater extents, the polydispersity index should attain a value of 2 according to theory. This is confirmed by the calculations. Thus, PDI of the product is relatively unaffected by the backmixing in the top portion of the column.

Tables 3 and 4 and Figs 5-11 show the results obtained for the sets of temperatures 240-253.5-265°C and 250-260-270°C.

3.2 Effect of Temperature

Temperature has a very interesting but predictable effect on the two-phase zone results. Tables 2 and 3 show that the conversions for 240-253.5-
265°C are higher than for 230-240-253.5°C. However, when compared with the results for 240-253.5-265°C, the conversions are lower for the set 250-260-270°C. These results can be rationalized once the rate accelerating effects of water and temperature are understood. At higher temperatures, the water-holding capacity of the streams is low (Tables 2-4). Thus, the decreased water contents tend to lower the rates as temperature is increased. However, as temperature is increased the rate of the reactions would increase. Thus, the two opposing effects produce a maximum in the conversion at an intermediate range of temperatures.

Figs 3-11 show the effect of temperature in the two-phase zone on the final product properties. It is observed that for \( \alpha = 1 \), the DPs achieved at 230-240-253.5°C, 240-253.5-265°C and 250-260-270°C are 157, 180 and 212 respectively. The conversions achieved are roughly the same. One can easily see the disparity in the final product produced. The difference in the product properties is also partly due to the fact that the PFR was assumed to be at the temperature of the last tank. To eliminate this effect, PFR calculations were also made assuming that the PFR was maintained at 253.5°C. From this calculation, the DPs achieved at roughly the same conversion for \( \alpha = 1 \) were 155, 178 and 225 for 230-240-253.5°C, 240-253.5-265°C and 250-260-270°C respectively. Clearly, the temperatures employed in the tanks affect the properties of end products very significantly. It might be noted that lowering of temperature would naturally result in increased residence time to reach the same conversions.

### 3.3 Effect of Rate Constants

Two sets of rate and equilibrium constants can be used in solving the modelling equations. The results for the case when Reimschuessel's rate
4 Conclusions

A stagewise model with backmixing has been developed to simulate polymerization in the top portion of a VK column reactor. The results indicate that backmixing in the top portion of the reactor affects the properties of the final product significantly. Increased backmixing leads to decreased degree of polymerization of the final product but a slightly higher monomer conversion. The temperatures employed in the top portion also have a significant effect on the end product properties. Increased temperatures in the top portion lead to higher degrees of polymerization.

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References

2. Jacobs H & Schweigman C, Mathematical model for the polymerization of caprolactam to nylon-6, paper presented at the fifth European/second international symposium on chemical reaction engineering, Amsterdam, 2-4 May 1972.

Appendix 1—Rate Expressions

\[
\frac{dM}{dt} = r_{m} = -k_{1} \left( MW-S_{m}/K_{1} \right) - k_{3}(MC-(C-S_{1})/K_{3})
\]

\[
\frac{dS_{1}}{dt} = r_{n} = -k_{1} \left( MW-S_{m}/K_{1} \right) - 2k_{2} [CS_{1} - W(C-S_{1})/K_{2}]
\]

\[\quad - K_{4}(MS_{1}-S_{1}/K_{4}) - K_{5}(C_{6}S_{1}-S_{1}/K_{5})\]

\[
\frac{dS}{dt} = r_{n} = K_{2} \sum_{n=1}^{\infty} S_{n} - m + 2 \left( \frac{k_{2}}{K_{2}} \right) W \sum_{m=1}^{\infty} S_{m}
\]

\[\quad - 2k_{2} CS_{n} - \left( \frac{k_{2}}{K_{2}} \right) W(n-1) S_{n} + k_{3}M(S_{n-1} - S_{n})\]

\[\quad + \left( \frac{k_{3}}{K_{3}} \right) (S_{n+1} - S_{n}) - k_{4} (C_{6}S_{n} - S_{n+2}/K_{4})\]

\[\quad + \left[ k_{3} C_{2} S_{n+2} - \left( \frac{k_{3}}{K_{3}} \right) S_{n} \right]_{n+2} + k_{4} (C_{6} W - S_{n}/K_{4})\]

\[
\frac{dW}{dt} = r_{n} = -k_{1} \left( MW-S_{1}/K_{1} \right) + k_{3}(C^{2} - WZ/K_{3})
\]

\[\quad - k_{4} (C_{6} W - S_{a}/K_{4})\]

\[
\frac{dC}{dt} = r_{c} = \sum_{n=1}^{\infty} \frac{dS_{n}}{dt} = k_{1} \left( MW-S_{1}/K_{1} \right) - k_{3}(C^{2} - WZ/K_{3})
\]

\[\quad + k_{4} (C_{6} W - S_{a}/K_{4})\]

\[
\frac{dZ}{dt} = r_{t} = \sum_{n=1}^{\infty} (n-1) \frac{dS_{n}}{dt} = k_{1} \left( MW-S_{1}/K_{1} \right) - k_{3}(C^{2} - WZ/K_{3})
\]

\[\quad + k_{4} (C_{6} W - S_{a}/K_{4})\]

\[
\frac{dC_{a}}{dt} = r_{c} = -k_{4} (C_{6} W - S_{a}/K_{4}) - k_{3}(C_{6} C-(C-S_{1})-S_{2}/K_{3})\]

\[\quad + 2k_{3} C_{2} C-(C-S_{1})-S_{2}/K_{3}\]