

## Modeling and Analysis of an LDPE Autoclave Reactor with Axial Dispersion

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**ABSTRACT** - An axial dispersion model is developed for the slim reactor employed in the LDPE autoclave process so that imperfect mixing caused by large L/D ratio (10~20) may be quantified by Peclet number. The model is then used to investigate the effect of mixing on the reactor performance represented by the monomer conversion, the reactor temperature, the molecular weight, and the polydispersity. In addition, the existence of steady state multiplicity is identified with the initiator feed concentration or the feed temperature as the bifurcation parameter. The effects of the initiator feed concentration and the feed temperature are also examined.

### INTRODUCTION

Polyethylene is one of the most widely used polymer. One of the major industrial processes for the polymerization of ethylene is the high pressure process which yields low-density product as the result of short chain branching formation. This bulk polymerization technique for the high pressure process requires highly purified ethylene stream (99.9 %). The process pressure ranges somewhere between 1000 and 3000 atm and the reactor temperature between 100°C and 300°C.

Two major types of commercial reactor have evolved : the tubular reactor and the stirred autoclave reactor. There are two basic types of the autoclave reactors : (1) highly backmixed, such as Du Pont compact reactor and (2) less highly backmixed, such as ICI slim reactor and National Distillers Autoclave. The latter has a larger length-to-diameter ratio(10~20) than the compact reactor(2~4). Most of the slim reactors are partitioned into several compartments and have two or more ports for the injection of monomer and/or initiator. Therefore, its operation scheme is more flexible and it can produce a wider range of products.

For the mathematical description of the autoclave slim reactor the mixing-cell model has been employed by several authors[3,11,13]. In order to study the effect of mixing, however, the axial dispersion model might be more effective. The previous application of the axial dispersion model for the polymerization system has been focused on the analysis of long tubular reactors. For example, Agrawal and Han[1] and Yoon and Rhee[16] developed the axial dispersion model for the LDPE tubular reactor and investigated the effects of various process parameters including the degree of axial mixing.

The axial dispersion model for the autoclave slim reactor presents a two-point boundary value problem

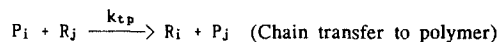
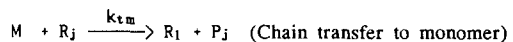
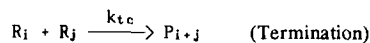
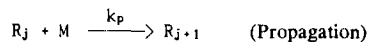
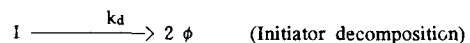
involving highly nonlinear reaction rate terms. Nonlinear system such as the LDPE autoclave reactor shows peculiar characteristics which include the steady state multiplicity and oscillatory behavior. Bifurcation analysis has been applied to such nonlinear systems. For example, Warden and Amundson[15] studied the steady state multiplicity and stability of a free radical polymerization system in a CSTR and Ray et al.[6,12] treated the solution polymerization system in a CSTR.

A distributed parameter system such as axial dispersion model is described by one or more ordinary differential equations, and also tractable to the bifurcation analysis. This has been demonstrated by various authors for the tubular reactor with axial dispersion, in which first order irreversible reaction takes place, by investigating various steady state and dynamic features; i.e., the uniqueness of the steady state solution[9,10], the oscillatory behavior[7], and the analytical treatment of simplified model[14].

In the present study it is intended to develop an axial dispersion model for the autoclave slim reactor in order to quantify the degree of mixing and investigate its effect on the reactor performance. By employing the bifurcation analysis, we also examine the effects of operating conditions on the reactor performance as well as on the properties of the polymer product.

### MODEL DEVELOPMENT

The free-radical polymerization mechanism[5] is adapted to ethylene polymerization and the following set of elementary reactions are to be considered:



Above elementary reactions are considered irreversible, and I,  $\phi$ , M,  $R_j$  and  $P_j$  represent the species of initiator, free radical, monomer, living polymer and dead polymer, respectively. These symbols will also be used to denote the concentration of the respective species.

Table 1. Reaction Rate Constants (P:atm)

REACTION	FREQUENCY FACTOR (s <sup>-1</sup> , l/mol · s)	ACTIVATION ENERGY (cal/mol)
INITIATION (TPA)	1.396 × 10 <sup>13</sup> , k <sub>d0</sub>	30102.8, E <sub>d</sub>
PROPAGATION	1.000 × 10 <sup>6</sup> , k <sub>p0</sub>	5864.2-0.516P, E <sub>p</sub>
TERMINATION	3.000 × 10 <sup>8</sup> , k <sub>t0</sub>	3950, E <sub>t</sub>
MONOMER TRANSFER	3.000 × 10 <sup>4</sup> , k <sub>t,m0</sub>	9375.2-0.48P, E <sub>t,m</sub>
POLYMER TRANSFER	1.000 × 10 <sup>6</sup> , k <sub>t,p0</sub>	11778.2-0.48P, E <sub>t,p</sub>

It is assumed that temperature dependence of the reaction rates may be expressed by the Arrhenius equation and the reaction rates are independent of the chain length except for the case of chain transfer to polymer. The chain length dependence of the reaction rate of the chain transfer to polymer may be expressed as

$$r_{t,p} = k_{t,p} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (b + i) R_j P_i$$

$$= k_{t,p} G (b F + F') \quad (1)$$

where b is the correction factor to be determined by experiment, and its value is proposed to be 1200 by Feucht et al.[4] The parameters for the reaction rate constants are taken from the literature and their numerical values are listed in Table 1.

The property of polymer product may be represented by the number and weight average molecular weight which are defined as

$$M_n = \frac{G' + F'}{G + F} \quad M_w = \frac{G'' + F''}{G' + F'} \quad (2)$$

where G, F, G', F', G'' and F'' are determined by

$$G = \sum_{j=1}^{\infty} R_j \quad F = \sum_{j=1}^{\infty} P_j$$

$$G' = \sum_{j=1}^{\infty} j R_j \quad F' = \sum_{j=1}^{\infty} j P_j \quad (3)$$

$$G'' = \sum_{j=1}^{\infty} j^2 R_j \quad F'' = \sum_{j=1}^{\infty} j^2 P_j$$

The end use properties of the produced polymer depend not only on the average molecular weights but also on the molecular weight distribution which may be characterized by the polydispersity which is defined as follows:

$$PD = M_w/M_n \quad (4)$$

Adiabatic reactor for ethylene polymerization is completely described by mass balances of the monomer, the initiator, the living polymer and the dead polymer, the moment equations for the living polymer and the dead polymer, and the energy balance. These equations may be written as

$$\frac{1}{Pe} \frac{d^2 y_i}{dz^2} - \frac{dy_i}{dz} + \bar{v}_i = 0 \quad (5)$$

for  $i = 1, 2, \dots, 9$ , where  $y_i$ 's are the dimensionless

Table 2. Dimensionless Groups

$z = x/L$	$\alpha = I_f/M_f$			
$y_1 = 1-I/I_f$	$y_2 = 1-W/M_f$	$y_3 = T/T_f$		
$y_4 = G/M_f$	$y_5 = G'/M_f$	$y_6 = G''/M_f$		
$y_7 = F/M_f$	$y_8 = F'/M_f$	$y_9 = F''/M_f$	$y_{10} = F'''/M_f$	
$\gamma_d = \frac{E_d}{RT_f}$	$\gamma_p = \frac{E_p}{RT_f}$	$\gamma_t = \frac{E_t}{RT_f}$	$\gamma_{t,m} = \frac{E_{t,m}}{RT_f}$	$\gamma_{t,p} = \frac{E_{t,p}}{RT_f}$
$Da_i = k_{d0} e^{-\gamma_d} \theta$	$Da_p = M_f k_{p0} e^{-\gamma_p} \theta$			
$Da_t = M_f k_{t0} e^{-\gamma_t} \theta$	$Da_{t,m} = M_f k_{t,m0} e^{-\gamma_{t,m}} \theta$			
$Da_{t,p} = M_f k_{t,p0} e^{-\gamma_{t,p}} \theta$	$B_p = (-\Delta H_p)M_f/\rho C_p T_f$			
$Pe_M = uL/D_M$	$Pe_H = uL/D_H$			

Table 3. Dimensionless reaction rates

$\bar{v}_1 = (1-y_1) Da_i \exp\{\gamma_d(y_3-1)/y_3\}$
$\bar{v}_2 = 2 \alpha f (1-y_1) Da_i \exp\{\gamma_d(y_3-1)/y_3\}$ $+ (1-y_2) y_4 Da_p \exp\{\gamma_p(y_3-1)/y_3\}$ $+ (1-y_2) y_4 Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$
$\bar{v}_3 = (1-y_2) y_4 Da_p B_p \exp\{\gamma_p(y_3-1)/y_3\}$
$\bar{v}_4 = y_4^2 Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $- 2 \alpha f (1-y_1) Da_i \exp\{\gamma_d(y_3-1)/y_3\}$
$\bar{v}_5 = 2 \alpha f (1-y_1) Da_i \exp\{\gamma_d(y_3-1)/y_3\}$ $+ (1-y_2) y_4 Da_p \exp\{\gamma_p(y_3-1)/y_3\}$ $- y_4 y_5 Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $+ (1-y_2)(y_4-y_5) Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$ $+ (by_4y_8+y_4y_9-by_5y_7-y_5y_8) Da_{t,p} \exp\{\gamma_{t,p}(y_3-1)/y_3\}$
$\bar{v}_6 = 2 \alpha f (1-y_1) Da_i \exp\{\gamma_d(y_3-1)/y_3\}$ $+ (1-y_2)(2y_5+y_4) Da_p \exp\{\gamma_p(y_3-1)/y_3\}$ $- y_4 y_6 Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $+ (1-y_2)(y_4-y_6) Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$ $+ (by_4y_9+y_4y_{10}-by_6y_7-y_6y_8) Da_{t,p} \exp\{\gamma_{t,p}(y_3-1)/y_3\}$
$\bar{v}_7 = \frac{1}{2} y_3^2 Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $+ (1-y_2) y_3 Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$
$\bar{v}_8 = y_4 y_5 Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $+ (1-y_2) y_5 Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$ $+ (by_5y_7+y_5y_8-by_4y_8-y_4y_9) Da_{t,p} \exp\{\gamma_{t,p}(y_3-1)/y_3\}$
$\bar{v}_9 = (y_4y_6 + y_5^2) Da_t \exp\{\gamma_t(y_3-1)/y_3\}$ $+ (1-y_2) y_6 Da_{t,m} \exp\{\gamma_{t,m}(y_3-1)/y_3\}$ $+ (by_6y_7+y_6y_8-by_4y_9-y_4y_{10}) Da_{t,p} \exp\{\gamma_{t,p}(y_3-1)/y_3\}$

quantities defined in Table 2. In Eq.(5), Pe is the dimensionless parameter which is defined by the ratio of the rate of bulk flow and that of axial dispersion, and  $\bar{v}_i$  defined in Table 3 denotes the dimensionless rates of generation of the quantity  $y_i$ . In Table 3,  $y_{10}$  is the third moment of the dead polymer and expressed explicitly by

Table 4. Thermodynamic Data and Conditions for the Reference System

$\rho$	413	g/l
$C_p$	0.518	cal/g · K
$\Delta H_p$	- 21400	cal/gmol
$I_f$	$5.0 \times 10^{-4}$	mol/l
$M_f$	14.75	mol/l
$T_f$	20	°C
$\theta$	18	sec
$P$	1200	atm
$Pe$	0.1 , 0.3 , 0.5	
$f$	0.453	

the first and second moments of the dead polymer using moment closure equation proposed by Hulburt and Katz[10].

$$y_{10} = \frac{y_9}{y_7 y_8} ( 2 y_7 y_9 - y_8^2 ) \quad (6)$$

Other parameters appearing in Table 3 are given in Table 2.

The boundary conditions to Eq.(5) are given by the Danckwerts conditions: i.e.,

$$y_i = \frac{1}{Pe} \frac{dy_i}{dz} \quad \text{at } z=0 \quad (\text{for Mass Balance})$$

$$1 - y_3 = - \frac{1}{Pe} \frac{dy_3}{dz} \quad \text{at } z=0 \quad (\text{for Energy Balance})$$

$$dy_i/dz = 0 \quad \text{at } z=1 \quad (7)$$

Thermodynamic data and conditions for the reference system are listed in Table 4.

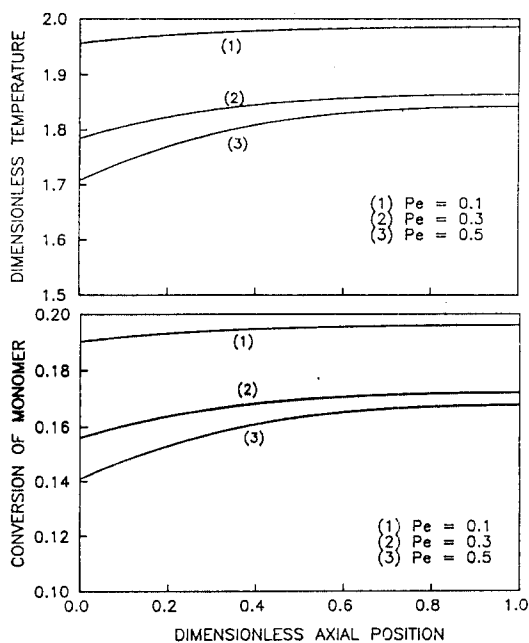


Fig.1 Profiles of the temperature and the monomer conversion for various Peclet numbers(reference system).

## RESULTS AND DISCUSSION

### Analysis of the reference system

Orthogonal collocation method was used to solve the system given by Eqs.(5) and (7). The temperature and the monomer conversion profiles of the reference system are given in Fig.1. The exit conversion of monomer ranges from 16 % to 20 %. The temperature profile for the case of  $Pe=0.3$  is in good agreement with typical plant data.

As the degree of axial dispersion increases, i.e. the Peclet number decreases, the temperature and the monomer conversion profiles become more diffuse as may be expected. Both the exit temperature and the exit monomer conversion decrease as Peclet number increases, since in this adiabatic system the efficiency of heat removal would be lower with larger Peclet number.

One may be tempted to increase the degree of mixing for higher conversion. According to the model analysis, however, the degree of mixing exercises a significant influence upon the properties of the polymer product as we shall see later. Therefore, it is necessary to have detailed analysis before making final decision.

### Effect of the Initiator feed Concentration

Bifurcation analysis may be applied to a nonlinear distributed parameter system in order to investigate the effects of various process parameters. For the given values of the parameters listed in Table 4, the steady state solution of Eq.(5) can be continuously computed, as the initiator feed concentration changes, by using the AUTO[2] which is a package program for the bifurcation analysis of algebraic and differential systems. Detailed numerical

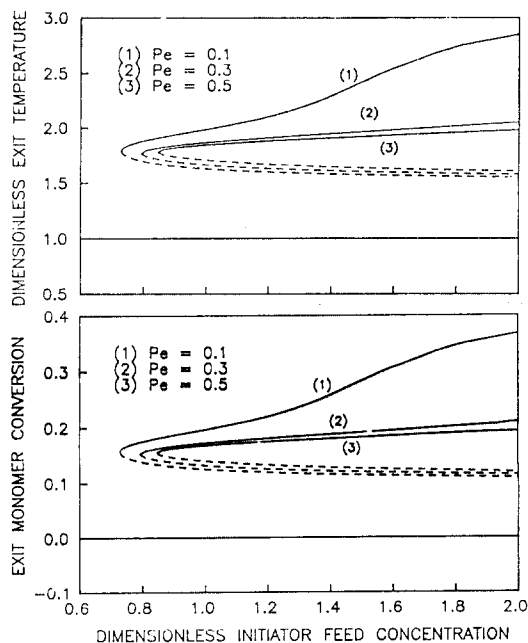


Fig.2 Bifurcation diagrams of the exit temperature and the exit conversion of monomer showing the effect of the initiator feed concentration for various Peclet numbers.

scheme for the bifurcation analysis of a distributed parameter system has been presented by several authors[7,9,10].

The bifurcation diagrams for three different values of  $Pe$  are shown in Fig.2. Here the diagram is drawn for the exit temperature and the exit monomer conversion with the initiator feed concentration as the bifurcation parameter. Clearly, the steady state multiplicity exists and the reactor system may have three different steady states for the particular range of initiator feed concentration.

The unstable middle branch(dashed line) lies between the stable upper and lower branches(solid line). The polymerization reaction may proceed only on the stable upper branch, along which the exit temperature and the exit monomer conversion increase with the initiator feed concentration. However, there would be an upper bound due to the allowable temperature limit and also a lower bound because of the existence of a turning point.

The three steady state profiles of the temperature and the monomer conversion are computed for the reference system with  $Pe=0.3$  and presented in Fig.3.

The bifurcation diagrams for the number average molecular weight and the polydispersity are shown in Fig.4. The stable branch that corresponds to the low conversion branch of Fig.2 falls in the range of very high molecular weight(above 50,000). It is interesting to note that the polydispersity approaches a limiting value of 2 irrespective of  $Pe$  when the conversion is extremely low.

Along the stable branches of practical interest, the number average molecular weight steadily decreases with

the initiator feed concentration whereas the polydispersity increases first and then decreases as the initiator feed concentration increases

As the Peclet number increases, both the exit temperature and the exit monomer conversion decrease while the molecular weight increases. One may note that the turning point shifts toward the higher initiator feed concentration as the Peclet number increases so that, with less mixing, more initiator needs to be supplied to obtain the same conversion.

#### Effect of the feed Temperature

In order to examine the effect of the feed temperature on the reactor performance, bifurcation diagrams are constructed with the feed temperature as the bifurcation parameter as shown in Fig.5 and 6. Here again we observe that the curve consists of three branches for each value of the Peclet number, so three different steady states are possible if the feed temperature falls in certain range.

Along the upper stable branch on which actual reactor conditions are expected to fall, the exit temperature steadily increases with the feed temperature regardless of the Peclet number. On the other hand, the exit monomer conversion tends to decrease with the feed temperature if the Peclet number is greater than 0.3. Such an unusual behavior may be explained as follows. As the feed temperature rises, the rate of generation of the free radical near the entrance of the reactor increases. When the Peclet number is larger than some critical value, the degree of mixing would not be sufficiently high so that

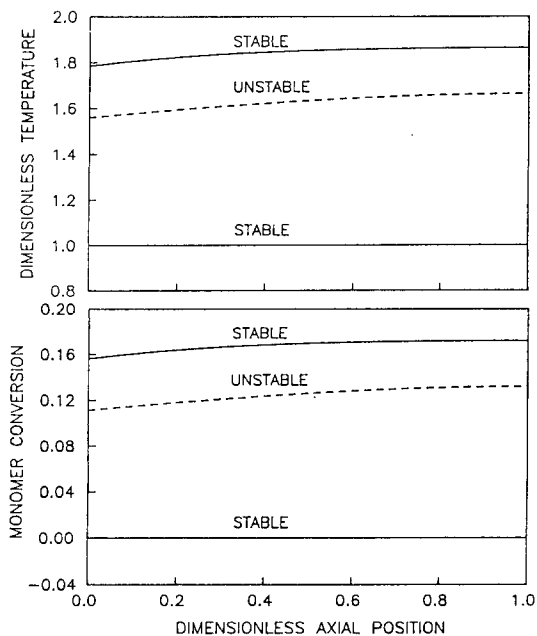


Fig.3 Profiles of the temperature and the monomer conversion at three different steady state for  $Pe=0.3$

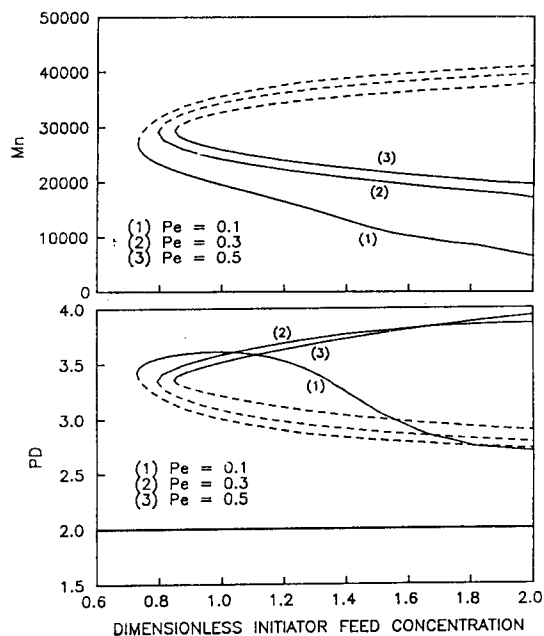


Fig.4 Bifurcation diagrams of the number average molecular weight and the polydispersity showing the effect of the initiator feed concentration for various Peclet numbers.

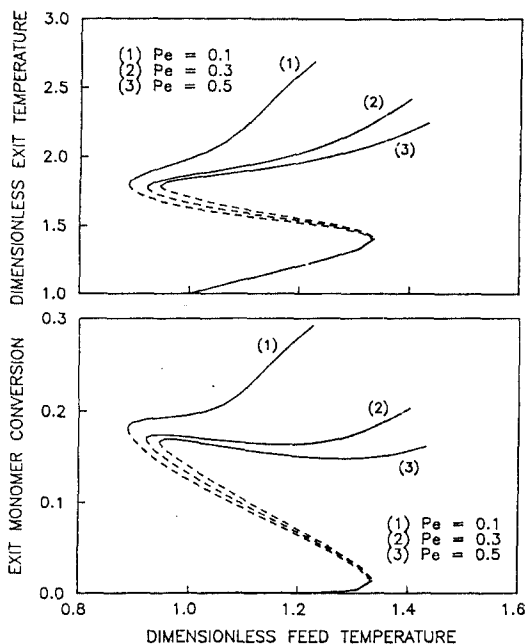


Fig.5 Bifurcation diagrams of the exit temperature and the exit conversion of monomer showing the effect of the feed temperature for various Peclet numbers.

free radicals generated may not have enough chance to take part in the polymerization reaction. Since the initiator feed rate is fixed, it is expected that the rate of polymerization would decrease and this entails a decrease in the monomer conversion.

Both the number average molecular weight and the polydispersity are found to decrease as the feed temperature increases. If the Peclet number is very small (See the curve for  $Pe=0.1$ ), the polydispersity appears to be very sensitive to the change in the feed temperature. This implies that the properties of the polymer product may be well controlled by regulating the feed temperature: for instance, the molecular weight distribution could be made narrow by increasing the feed temperature.

### CONCLUSION

Axial dispersion model is proven adequate for predicting the performance of the slim reactor used in the LDPE autoclave process. The degree of mixing represented here by the Peclet number has a significant effect on the reactor performance. Thus mixing is required for high conversion but one must take into account the fact that the properties of the polymer product may also be influenced.

Bifurcation analysis shows that the reactor system, which is a distributed parameter system, can have up to three different steady states. Among the three, however, only one is of practical interest and its state has an upper bound due to the temperature limit and a lower bound because of the existence of the turning point.

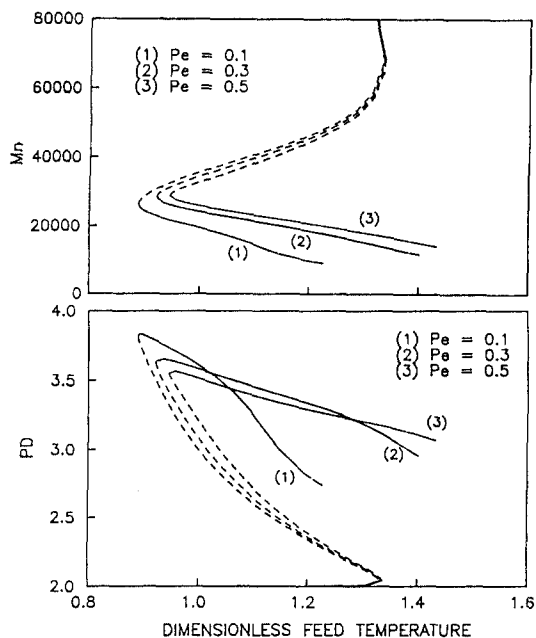


Fig.6 Bifurcation diagrams of the number average molecular weight and the polydispersity showing the effect of the feed temperature for various Peclet numbers.

As the initiator feed concentration increases, both the exit temperature and the exit monomer conversion tend to increase and, while the number average molecular weight steadily decreases, the polydispersity takes a maximum.

Unless the Peclet number is very small, the exit monomer conversion slightly decreases with the feed temperature while the exit temperature increases. This might be caused by inefficient mixing of free radicals near the entrance of the reactor. An increase in the feed temperature makes both the number average molecular weight and the polydispersity decrease.

As the Peclet number becomes larger, it is required to have a higher initiator feed concentration or a higher feed temperature to attain the same level of monomer conversion. When the monomer conversion becomes extremely low, the polydispersity approaches a limiting value of two as expected.

### NOTATION

$C_p$	: Heat capacity of reaction mixture	[cal/g °C]
$D_H$	: Axial heat dispersion coefficient	[m <sup>2</sup> /s]
$D_M$	: Axial mass dispersion coefficient	[m <sup>2</sup> /s]
$E$	: Activation energy	[cal/mol]
$f$	: Initiator efficiency	
$\Delta H_p$	: Heat of polymerization	[cal/mol]
$I$	: Initiator concentration	[mol/l]
$k$	: Reaction rate constant	[s <sup>-1</sup> , l/mol.s]
$k_0$	: Pre-exponential factor	[s <sup>-1</sup> , l/mol.s]
$L$	: Reactor length	[m]
$M$	: Monomer concentration	[mol/l]
$P$	: Reactor pressure	[atm]

$P_j$  : Dead polymer species of chain length  $j$   
 $R_j$  : Living polymer species of chain length  $j$   
 $T$  : Reactor temperature [K]  
 $u$  : Linear velocity of fluid [m/s]  
 $x$  : Axial position [m]

Greek letters

$\theta$  : Reactor mean residence time [s]  
 $\rho$  : Density of reaction mixture [g/l]  
 $\phi$  : Free radical

Subscripts

$d$  : Initiator decomposition  
 $f$  : Feed condition  
 $j$  : Chain length of living polymer and dead polymer  
 $p$  : Propagation  
 $t$  : Termination  
 $tm$  : Chain transfer to monomer  
 $tp$  : Chain transfer to polymer

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