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MATHEMATICAL MODEL AND ANALYSIS OF PMMA SOLUTION PROCESSES

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Abstract – A mathematical model of reactors for the polymerization of methylmethacrylate (MMA) has been developed and analyzed in order to better understand the reactor dynamics and to determine conditions for improved operation. The exploration of the effect of heat transfer in an MMA polymerization reactor system has been conducted by the development of a detailed model. Two correlations for the overall heat transfer coefficient have been used to study the effect of heat transfer. The heat transfer coefficient estimated by an empirical correlation (Kravaris) is only a function of conversion. Due to its simplicity, it may not express very well the true heat transfer phenomena. But in Henderson's correlation, it is related to the viscosity of the reaction mixture, which in turn depends on the reaction temperature and volume fraction of each species in the reactor. The steady state solutions of mass and energy balances in the reactor depend on the nature of the heat transfer correlation, as does the number of isola branches. Henderson's correlation may be preferred to calculate the dynamics of the PMMA reactors. The addition of jacket dynamics to the system results in no isola solution branches and no Hopf bifurcations.

Key words: Polymerization, Dynamics, Bifurcation, Stability, Reactor

INTRODUCTION

The polymerization reaction of MMA is highly exothermic (heat of reaction=13.8 kcal/mol). In order to avoid a hot spot or thermal runaway, a reactor is normally cooled. Hewitt et al. [1994] discuss several methods for heat transfer in agitated vessels and show that heat transfer [specifically, the overall heat transfer coefficient (OHTC)] depends on the design specifications of the agitator. Though heat transfer to a coolant is very important in MMA polymerization, most earlier works have assumed a constant OHTC. Some researchers, however, have derived empirical correlations between the OHTC and monomer conversion and have shown the impact of a varying OHTC on reactor performance and dynamics. The figures in Kim and Laurence's paper [1997] show that reaction temperature changes dramatically with increasing reactor residence time. We may conclude that the assumption of a constant OHTC is inappropriate and may not explain the actual dynamics of MMA polymerization.

In this work, we derive the equations describing mass and energy balances in the reactor. Some assumptions used in prior work are not included. Two correlations of the OHTC, that is, the relationship of the OHTC with monomer conversion and with temperature and viscosity, are described in section 2. Their effect on reactor dynamics is discussed in section 3 and the conclusion follows.

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GOVERNING EQUATIONS AND OVERALL HEAT TRANSFER COEFFICIENT

The importance of heat transfer in MMA polymerization has already been discussed. Since the reaction temperature changes with varying reactor residence time, the OHTC is not constant and a correlation for the OHTC must be included in the energy balance. Two correlations are used in this work. One method (we will call it "method 1") is based on the relation between monomer conversion and OHTC. Chylla and Hasse [1993] developed an empirical correlation to relate OHTC to the viscosity of the reaction mixture, also related to conversion and temperature. Takamatsu et al. [1987] proposed an empirical correlation in which the OHTC is a function of conversion. Soroush and Kravaris [1992] used a correlation similar to Takamatsu et al. in a study of the control of batch polymerizations. They assumed that the OHTC is a function only of the monomer conversion.

Another method (we will call it "method 2") is based on the derivation of a correlation between the internal heat transfer coefficient and viscosity and physical properties of the mixture. Henderson [1987] used it in a study of the stability of styrene polymerization in a CSTR. He found that the OHTC falls from the initial value to an order of magnitude less in the laminar region, that is, where the Reynolds number is less than 100. Kim et al. [1992] studied the dynamics of a CSTR for styrene polymerization initiated by a binary initiator mixture with heat transfer to a jacket. They used the same correlation as in Henderson and showed that the dynamics is relatively simpler than that of the case assuming a constant OHTC. In this method, constitutive equations for viscosity and oth-

er physical properties, i.e., thermal conductivity and heat capacity, must be sufficiently accurate to describe the real reactor dynamics.

We compare these two correlations and show their effect on the reactor dynamics. We denote a correlation which slightly modifies the Soroush-Kravaris (SK) correlation as Method 1. The value of the OHTC that they prescribe at zero conversion is too small and unrealistic. To provide a basis for comparison with Method 2, we use the same value at zero conversion obtained from the Henderson correlation. However, it shows unrealistic reactor dynamics. Therefore, we use a zero concentration value slightly greater than that in Henderson. We choose the correlation used by Henderson as Method 2. The constitutive equation for viscosity developed by Baillagou and Soong [1985] is used in the correlation. This is given in Table 1. The governing equation and the forms of OHTC for method 1 and 2 are also shown in Table 1.

These two methods are based on the assumption of constant coolant temperature. Russo and Bequette [1992] have studied limitations on the CSTR performance due to cooling jacket dynamics. They used a classical exothermic CSTR [Ray, 1982] and found that the three states model (concentration, temperature and cooling temperature), which accounts for cooling jacket dynamics, may be open-loop unstable in regions where the two states model (concentration and temperature) is open-loop stable. However, they did not calculate a detailed bifurcation diagram and assumed that a dimensionless parameter containing the OHTC is constant. To study the effect of cooling dynamics on reactor dynamics, we use a correlation for the external heat transfer coefficient described in Hewitt et al. [1994] and include it in Table 2 (we call it Method 3). The governing equations including cooling jacket dynamics are also described in Table 2. The detailed derivation of the governing equations can be seen in Kim's work [1994]. Physical properties of materials used in the polymerization and kinetic constants are shown in Table 3 and 4, respectively.

Table 1. Mass and energy balances for a detailed model

$$V\frac{dM}{dt} = q_f M_f - qM - Vk_p M\lambda_0$$

$$V\frac{dI}{dt} = q_f I_f - qI - Vk_d I$$

$$\overline{\rho C_p} V\frac{dT}{dt} = \rho_M(T_f)\phi_{Mf} q_f C_{PM}(T_f - T) + \rho_S(T_f)\phi_{Sf} q_f C_{PS}(T_f - T) + (-\Delta H_p)Vk_p M\lambda_0 - UA_r(T - T_c)$$

$$V\frac{dS}{dt} = q_f S_f - qS$$

$$V\frac{d\lambda_0}{dt} = -q\lambda_0 + V(2fk_d I - k_t\lambda_0^2)$$

● Kravaris Empirical Correlation

$$U = U_0[\alpha + (1-\alpha)\exp(-bX^c)]$$

$$U_0 = U(X=0)$$

● Henderson's Correlation

$$Nu = 0.51\,Re^{2/3}Pr^{1/2}\left(\frac{\eta_r}{\eta_w}\right)^{0.14} \quad \text{if } Re>100$$

$$Nu = 0.51\,Re^{1/3}Pr^{1/3}\left(\frac{\eta_r}{\eta_w}\right)^{0.2} \quad \text{if } Re<100$$

$$\eta_p = \eta_m + 0.6\,D_p^{1.4}\exp\left(\frac{0.8}{ff}\right) \quad \text{for } D_p<0.13$$

$$\eta_p = \eta_m + 200\,D_p^{4.2}\exp\left(\frac{0.8}{ff}\right) \quad \text{for } D_p<0.13$$

$$\eta_m = \exp\left\{2.303\left(\frac{0.115}{0.025 + 10^{-3}(T_c + 106)} - 1\right)\right\}$$

$$ff = \{0.025 + 10^{-3}(T_c + 106)\}\phi_M + \{0.025 + 10^{-3}(T_c + 6180)\}\phi_s + \{0.025 + 0.48\times10^{-3}(T_c - 144)\}\phi_p$$

where $D_p = 1.2\phi_p$, $\overline{\rho C_p} = \rho_M C_{pM}\phi_M + \rho_s C_{ps}\phi_s + \rho_p C_{pp}\phi_p$

Table 2. Governing equations for the polymerization system including cooling jacket dynamics

$$\rho_c C_{Pc} V_c \frac{dT_c}{dt} = \rho_{cf} q_{cf} C_{Pc}(T_{cf} - T_c) + UA(T - T_c)$$

$$Nu_c = 0.023\,Re_c^{0.8}Pr_c^{0.4}$$

$$\frac{1}{U} = \frac{1}{h_I} + \frac{1}{h_o}$$

Table 3. Physical properties of materials in the polymerization of MMA

$\rho_M = 0.968 - 1.255\times10^{-3}T_c$	(g/cm^3)
$\rho_p = \rho_M(1+\varepsilon)$	(g/cm^3)
$\varepsilon = 0.183 + 9.0\times10^{-4}T_c$	
$\rho_s = 0.883 - 9.0\times10^{-4}T_c$	(g/cm^3)
$C_{PM} = 0.4$	(cal/g °C)
$C_{PP} = 0.339 + 9.55\times10^{-4}(T_c - 25)$	(cal/g °C)
$C_{PS} = 0.535$	(cal/g °C)
$M_{WM} = 100.13$	(g/mol)
$M_{WS} = 92.14$	(g/mol)
$(-\Delta H_r) = 13800$	(cal/mol)

Reactor and reactor medium constants

f = 0.8, U = 135 cal/m^{2}sK, Ar = 2.8 m^2

*T_c : T (°C)

Table 4. Kinetic constants for the MMA polymerization

$k_d = 6.32\times10^{16}\exp\left(-\frac{30.66\ (kcal/mol)}{RT}\right)$	$\left(\frac{l}{min}\right)$
$k_p^o = 2.95\times10^{7}\exp\left(-\frac{4.35\ (kcal/mol)}{RT}\right)$	$\left(\frac{l}{mol\ min}\right)$
$k_t^o = 5.88\times10^{9}\exp\left(-\frac{0.701\ (kcal/mol)}{RT}\right)$	$\left(\frac{l}{mol\ min}\right)$
$k_{tc} = k_{td}\cdot 3.956\times10^{-4}\exp\left(-\frac{4.09(kcal/mol)}{RT}\right)$	
$k_t = k_{tc} + k_{td}$	

(reference: Baillagou and Soong, 1985b)

TEMPERATURE BOUNDS IN POLYMERIZATION

In free radical polymerization, the propagation reaction is

the dominant step and is highly exothermic. Therefore, if the heat produced during reaction is not adequately removed from the reactor, thermal auto-acceleration may occur and the reactor becomes unstable. Molecular weight distribution and chain growth are also affected by variation of reaction temperature. In our work, as in most prior work, the propagation step is assumed irreversible. Some reference temperatures, i.e., critical and ceiling temperatures, are introduced to check the validity of this. Since MMA polymerization is a nonisothermal reaction and requires heat transfer to coolant, we introduce two reference temperatures to check thermal stability.

Free radical polymerization occurs spontaneously, that is, the free energy of the polymer chain is lower than that of the monomer. Therefore, the Gibbs free energy change, ΔG, is neg-

Table 5. Isola centers for a detailed model

(a) Method 1				(b) Method 2	
X_1=0.822465	X_2=0.134384	X_1=0.738473	X_2=0.766139	X_1=0.659693	X_2=0.682187
X_3=0.857308	X_4=1.0	X_3=1.82654	X_4=1.0	X_3=1.39364	X_4=1.0
X_5=2.56788×10^{-7}	Model=Detailed	X_5=4.78204×10^{-7}	Model=Detailed	X_5=5.18479×10^{-7}	Model=Detailed
θ=1.01954	T_F=313.932	θ=0.164531	T_F=315.017	θ=0.103577	T_F=329.224

(fixed parameters : I_F=0.05, M_F=5.0, S_F=4.7, T_C=T_F)

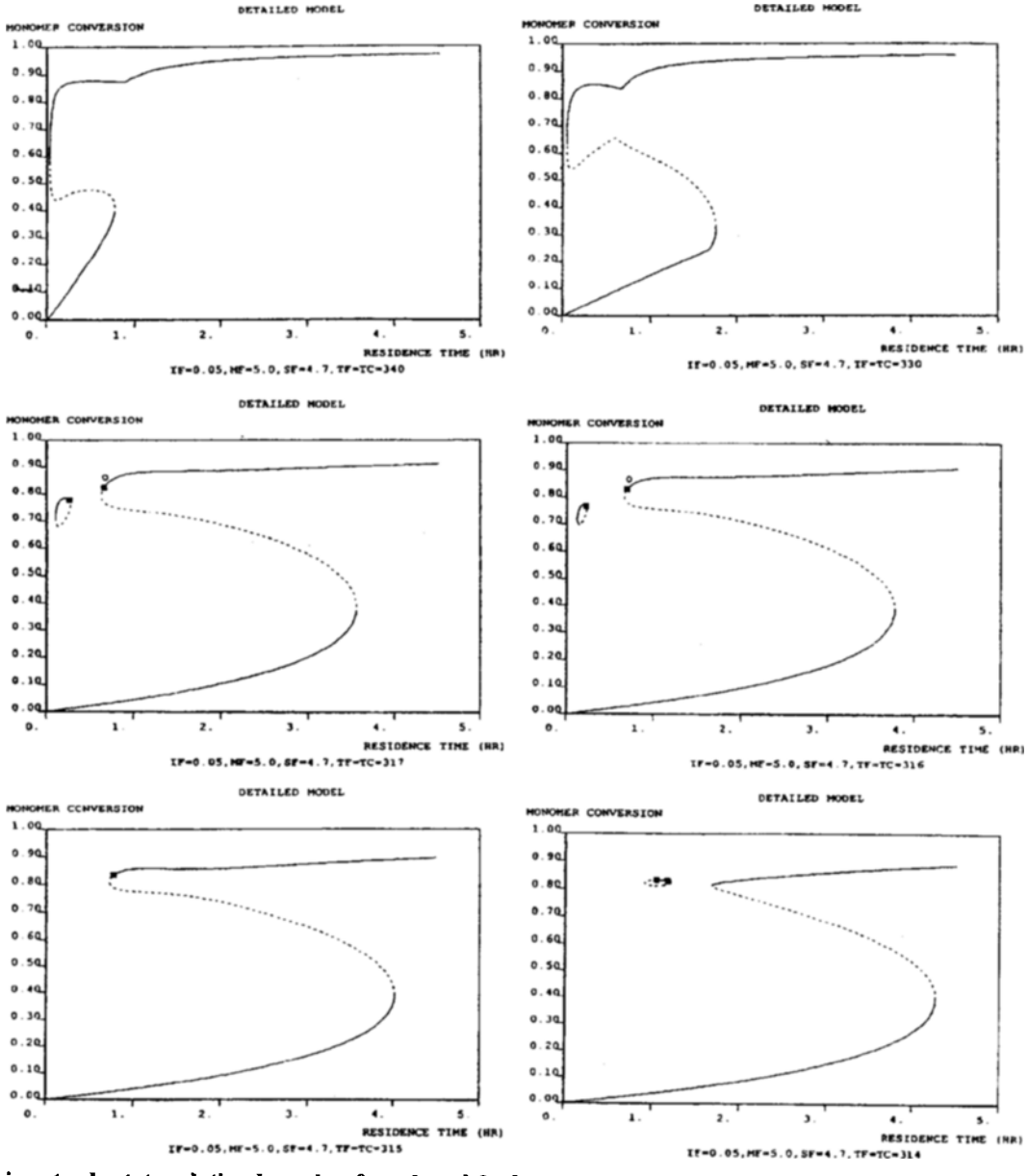

Fig. 1. Conversion steady state solution branches for selected feed temperatures in method 1 for a detailed model.
(—: stable, ---:unstable, ● :stable Hopf, ○ :unstable Hopf)

ative. If the reaction mixture is in equilibrium at that temperature, there is no polymerization and $\Delta G=0$. This temperature is called "Ceiling Temperature". At temperatures above this temperature, a depolymerization reaction exceeds polymerization. Using the definition of Gibbs free energy and the standard state, we define the Ceiling Temperature as

$$T_{ce} = \frac{\Delta\tilde{H}_r}{\Delta\tilde{S}_p^o + R \ln M} \tag{1}$$

where $\Delta\tilde{S}_p^o$ is the entropy change accompanying polymerization in the standard state.

The monomer concentration affects T_{ce}, but is independent of monomer type. Tobolsky and Eisenberg [1962] defined "Critical Reaction Temperature" as follows:

$$T_{cr} = \frac{\Delta\tilde{H}_r}{\Delta\tilde{S}_p^o + R \ln M_f} \tag{2}$$

The difference between T_{ce} and T_{cr} is that T_{ce} shows a locus of critical values, but T_{cr} is a single value. The critical reaction temperature represents the phenomenon that the production of polymer is impossible from the outset. The locus of ceiling temperatures indicates that, regardless of polymer produced prior to the approach of the critical condition, the polymer depolymerizes. Therefore, these two temperatures provide upper temperature limits to be avoided during a nonisothermal polymerization reaction.

To check the effects of heat transfer and polymerization on the reaction temperature, two additional temperatures, i.e., T_{ad} and T_x, may be defined by the following equations:

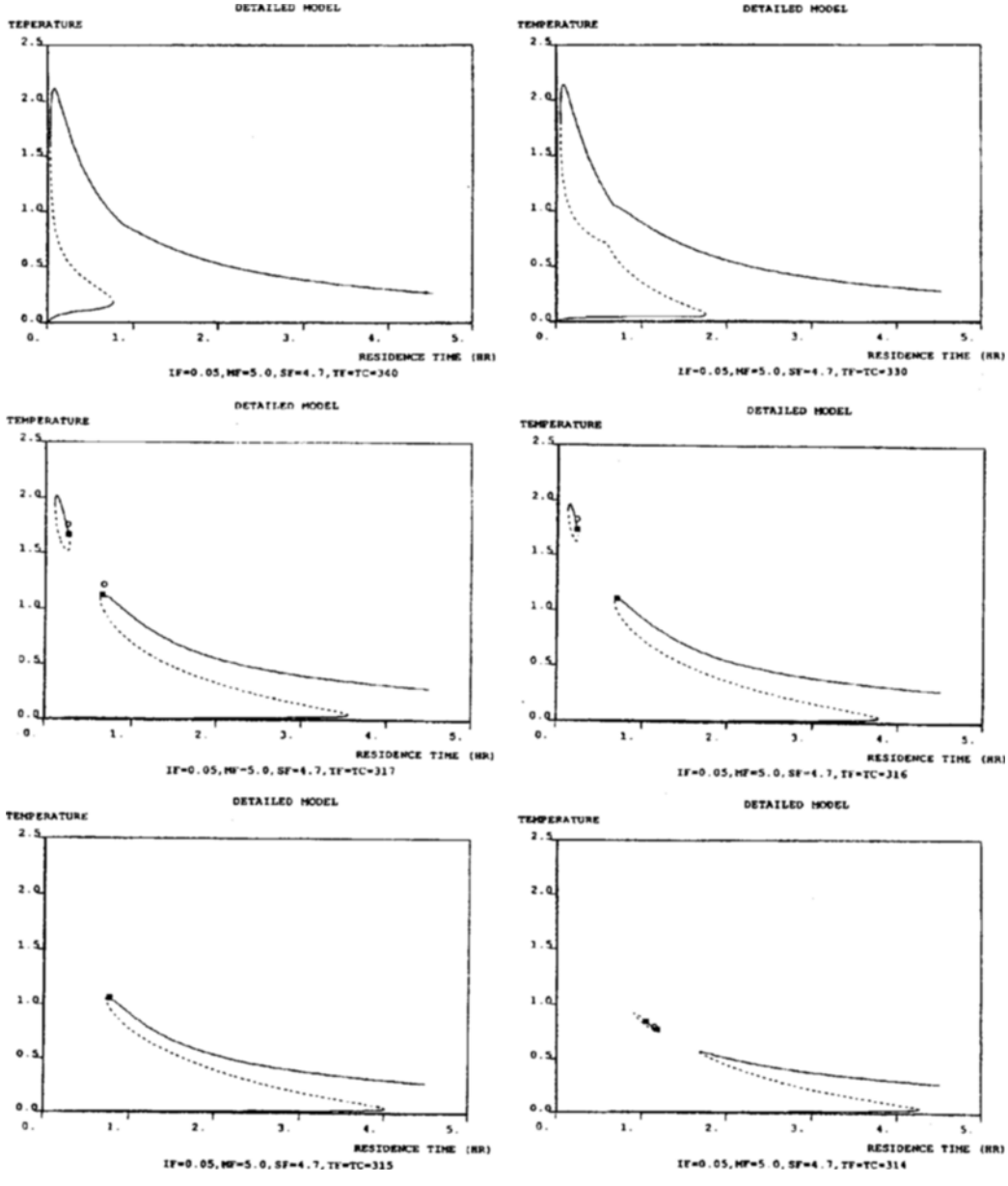

Fig. 2. Temperature solutions corresponding to the conversion branches in Fig. 1.

$$T_{ad} = \frac{(-\Delta\tilde{H}_r)M_f}{\overline{\rho C_p}} + T_f \tag{3}$$

$$\rho_M(T_f)\phi_{Mf}q_f C_{pM}(T_f - T_x) + \rho_s(T_f)\phi_{sf}q_f C_{ps}(T_f - T_x) = U(T_x)A(T_x - T_c) \tag{4}$$

The locus of the adiabatic reactor temperature, T_{ad}, and the temperature under the condition of no reaction, T_x, depends on the models developed in section 2. For example, in the simple model, $\overline{\rho C_p}$ is constant, but in the detailed model it depends on the species volume fractions. If the OHTC is not constant, the temperature under no reaction, T_x, has a locus that changes with residence time, in contrast to the case of constant OHTC.

RESULTS AND DISCUSSION

Contrary to the simple case in Kim and Laurence [1997], it is shown in method 1 that the position of one of the two isola centers appears at a residence time of approximately 1 hour at a feed temperature of 314 K. These two loci are shown in Table 5. At a higher feed temperature, T_f=340 K, the unstable steady state regions are broad when compared to those of the simple model. Two isola solution branches do not coexist in this case. When T_f decreases, one isola branch is cleaved from the upper branch of the sigmoidal curve and then disappears. If T_f decreases further, the second isola branch is pinched from the rest of the curve. Similar behavior is observed in the temperature diagrams. These are plotted in Fig. 1 and 2, respectively.

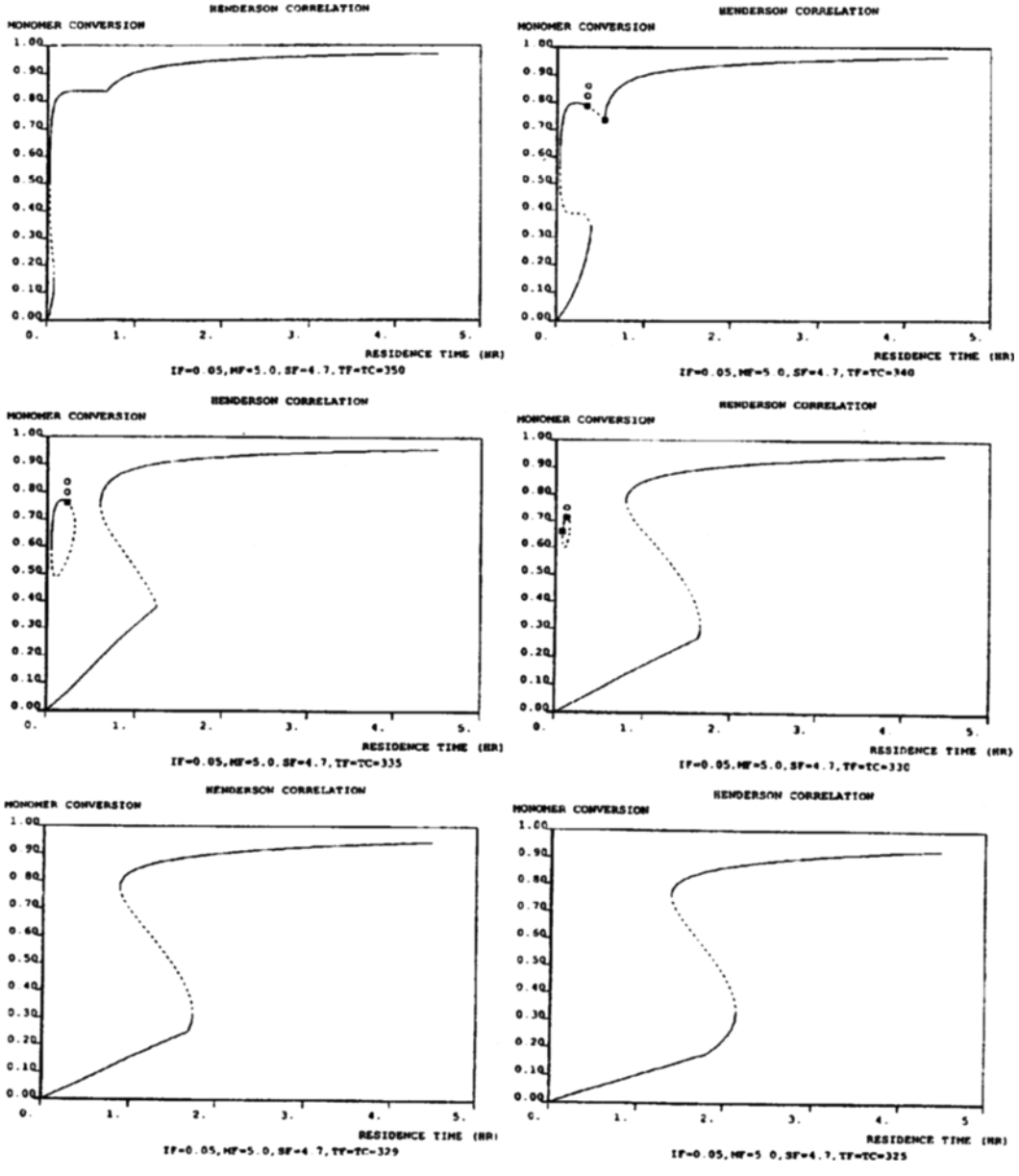

Fig. 3. Conversion steady state solution branches for selected feed temperatures in method 2 for a detailed model.

When we used the Henderson correlation with Soong's viscosity equation (method 2), only one isola solution branch was detected as the residence time changed (see Table 3). The feed temperature at which the isola center appears is much greater than in method 1 and in the simple model. When the feed temperature is decreased, the isola branch is cleaved from the upper solution curve and disappears. For further decrease in T_f, only the sigmoidal solution branch exists (Fig. 3). At feed temperatures below 329 K, the maximum reaction temperature is only about 70 °C (see Fig. 4). This differs from method 1 where the maximum reaction temperature is around 150 °C. Note that only the isola branch possesses a Hopf bifurcation. No Hopf bifurcation points exist on the sigmoidal curve, a very different result than that of method 1 where Hopf bifurcations exist on both the isola and the sigmoidal curve. We may conclude that the correlation of the OHTC really affects the reactor dynamics.

Surprisingly, in comparison with the cases of constant coolant dynamics, we found no isola branch as the residence time changes. Here, the coolant residence time was fixed at 1 hour. When feed and coolant temperatures are identical, most of the polymerization occurs at short residence time. The unstable steady state region increases with decreasing feed temperature, but the region is very small (Fig. 5). The difference between this case and the previous cases is evident when the reaction temperature profiles are compared. In the previous cases, the reaction temperature is decreased dramatically and levels off to a value of 0.5 as residence time changes. However, the reaction temperature, in this case, at greater reactor residence time is greater than 1.5. It is interesting to note that when the feed temperature is decreased, the peak reaction temperature and the profile are higher (see Fig. 6). The coolant temperature changes slightly with decreasing feed temperature and is shown in Fig. 6. The energy input from a cool-

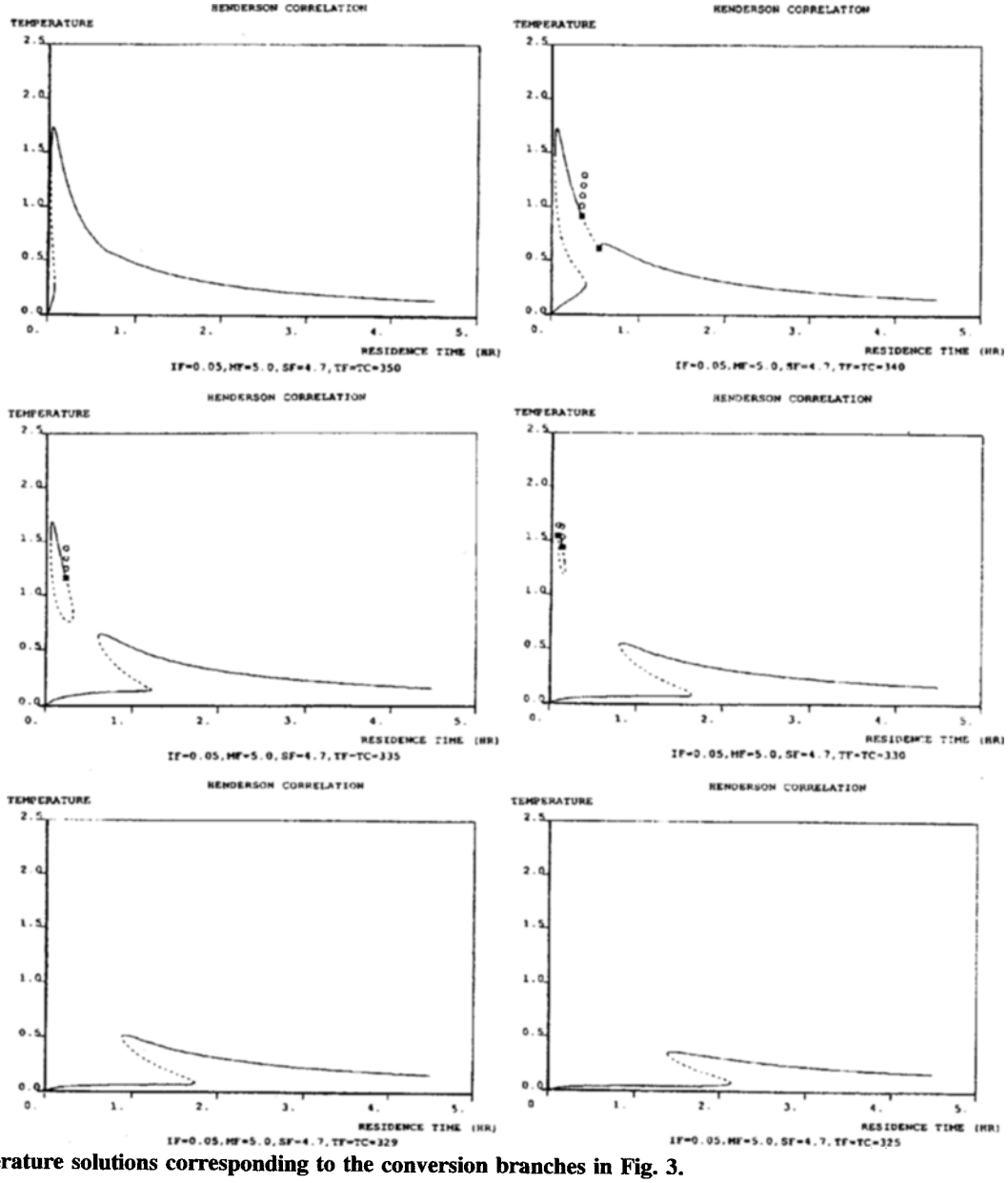

Fig. 4. Temperature solutions corresponding to the conversion branches in Fig. 3.

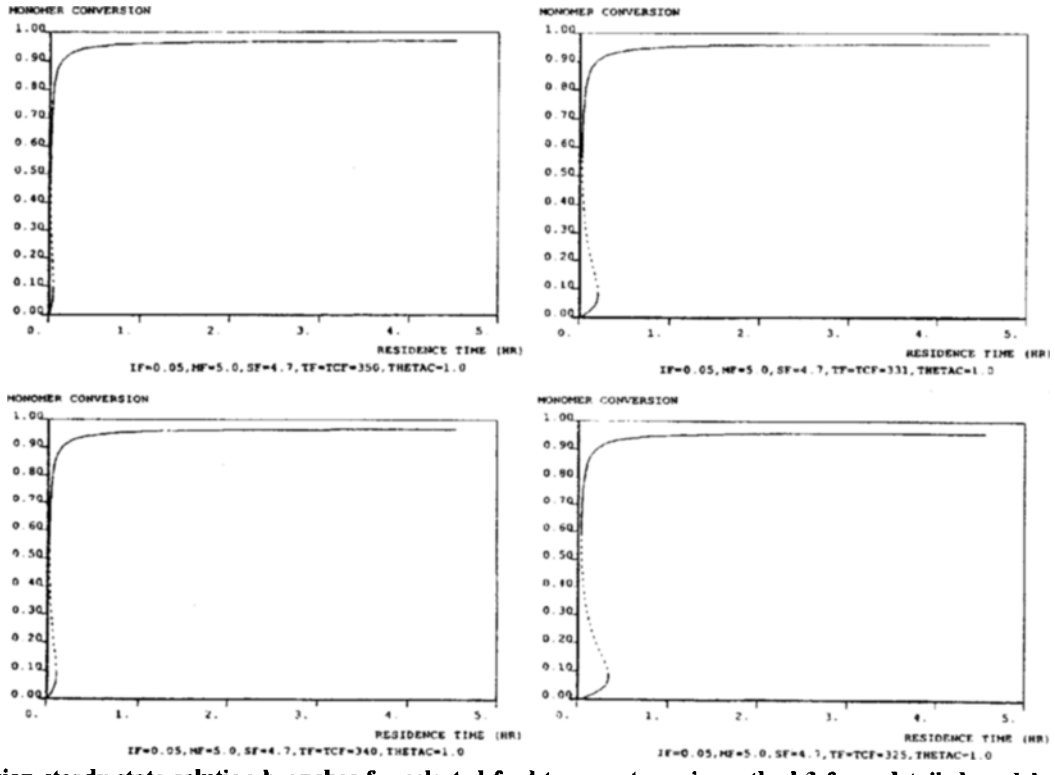

Fig. 5. Conversion steady state solution branches for selected feed temperatures in method 3 for a detailed model.

ant affects the reaction temperature profile. Note that no Hopf bifurcations exist.

The heat transfer coefficient estimated by an empirical correlation (Kravaris) is only a function of conversion, but in Henderson's correlation, it is related to the viscosity of the reaction mixture, which in turn depends on the reaction temperature and the volume fraction of each species in the reactor. When we add coolant jacket dynamics to the system, the OHTC is calculated from the relation shown in Table 2. The external heat transfer coefficient (EHTC) varies with the coolant jacket diameter and flow rate. Since volume fractions and reaction temperature vary as residence time changes, the Kravaris correlation may be the simpler correlation. Most phenomena such as viscosity changes are stored in correlation coefficients, which are necessarily obtained from experimental data. This may be a drawback for a dynamic analysis of the system. The Henderson correlation also has drawbacks, because it is not easy to establish an accurate relationship of viscosity to the number of parameters, such as temperature, pressure, shear rate, average molar mass, etc. A comparison of the values of the OHTC determined by each correlation (depicted in Fig. 7) shows that those values differ and depend on the type of correlation. Different values of the OHTC may be one reason for the different reactor dynamics. Note that the OHTC determined by using method 3 is lower than that in the other two methods, which means the transfer of heat to a coolant may be poorer. In Fig. 6, we note that the peak temperature is relatively higher. The value of the coolant residence time is 1 hr. If the flow rate increases, more heat would be transferred from the reactor. Accurate design parameters are required to show the real heat transfer phenomena in a commercial-scale reactor. However, these correlations do help us understand the heat transfer phenomena in the reactor. Kim et al. [1992] observed that the reactor system with a viscosity and a heat transfer coefficient (similar to the Henderson correlation) shows a simpler steady state and dynamic behavior for a styrene polymerization reactor with a binary initiator mixture. A similar phenomenon is observed here and we may conclude that the assumption of a constant OHTC may not be valid for modeling a nonisothermal polymerization reactor.

The profiles of the temperature bounds are shown in Fig. 8. We used the same data in the simple model as in the imperfect mixing model. In these two cases, the profiles of adiabatic reactor temperature and temperature under no reaction are constant regardless of residence time. The reaction temperature is always less than the ceiling temperature and the adiabatic reactor temperature. When we use Kravaris' correlation for the OHTC, the adiabatic temperature changes because density and heat capacity depend on the volume fractions of the reaction mixture. Similar phenomena are observed for the case of Henderson's correlation. A single isola branch is detected at a feed temperature of 330 K, and the ceiling and adiabatic temperatures have the same locus for an isola. The reaction temperature profiles, however, are bounded like a simple model case, regardless of the choice of correlation for the OHTC. The phenomenon is entirely different in the case of cooling dynamics. The reaction temperature at a residence time of about 0.2 to 1.8 hours is greater than the ceiling temperature. This implies that polymer production in that region is impossible and the assumption of irreversibility of the propagation reaction is no longer valid. It indicates that cooling

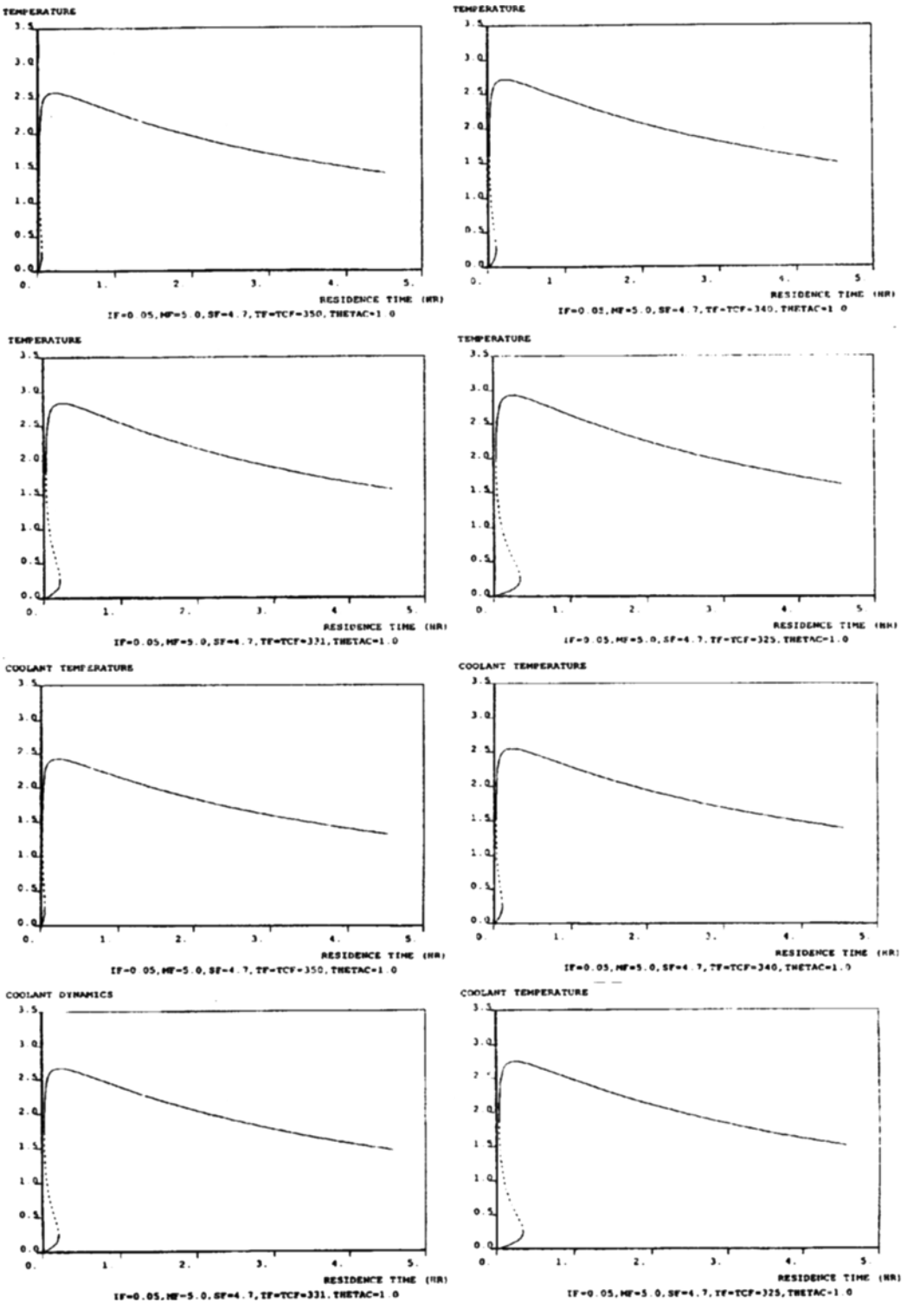

Fig. 6. Reactor and coolant temperature solutions corresponding to the conversion branches in Fig. 5.

jacket dynamics really affects the reactor dynamics and the use of the simple model may result in an inappropriate and infeasible operating region.

CONCLUSION

In order to develop a better understanding of the dynamics of MMA polymerization reactors, to better control polymer properties, and to improve productivity, a detailed model has been developed with fewer assumptions.

Using the first law of thermodynamics for open system, we derived an energy balance and noted that the physical properties of the reaction mixture are not constant, but functions of its volume fraction. Two correlations for overall heat trans-

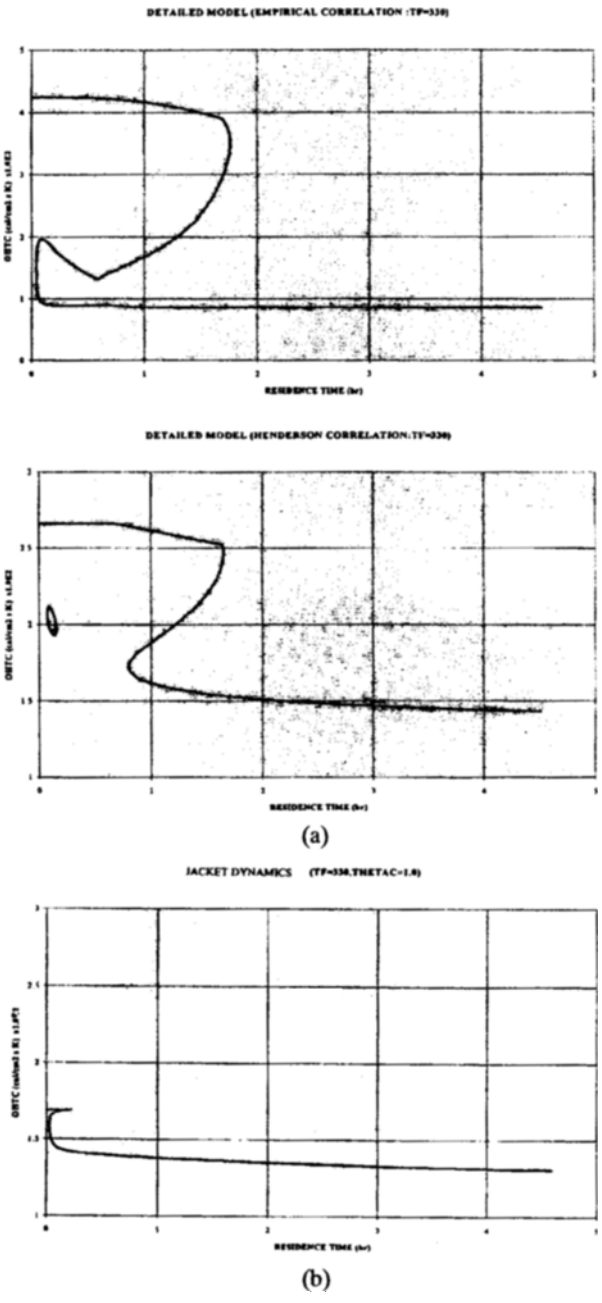

Fig. 7. A comparison of overall heat transfer coefficients.

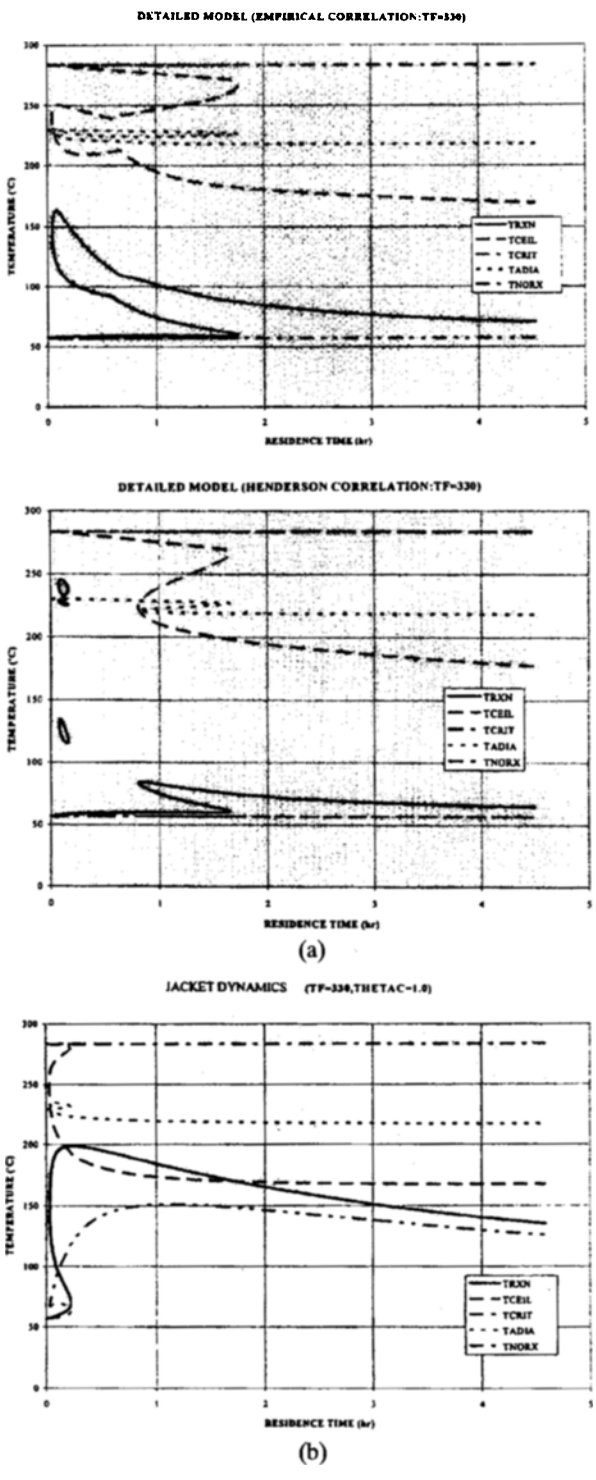

Fig. 8. Profiles of temperature bounds.

fer coefficient were compared to explore the transfer of heat in polymerization reactors. To study the effect of coolant jacket dynamics on the dynamics of a polymerization reactor, the equations governing the polymerization reactor with coolant dynamics were developed. The assumption of irreversibility of propagation reaction was checked using several redefined temperatures, such as ceiling, critical reaction, adiabatic, and temperature under no reaction.

1. The steady state solutions of the governing equations for mass and energy balances in the reactor and the number of isola branches do depend on the type of correlation. The solutions differ from those of a simple model.

2. The addition of coolant dynamics to the model results in no isola solutions and no Hopf bifurcation points.

3. The diagram of temperature bounds shows that the assumption of irreversibility of propagation reaction may not be valid at lower residence times.

The heat transfer coefficient estimated by an empirical correlation (Kravaris) is only a function of conversion. Due to its simplicity, it may not express very well the true heat trans-

fer phenomena. In Henderson's correlation, however, it is related to the viscosity of reaction mixture, which in turn depends on reaction temperature and volume fraction of each species in the reactor. When we add jacket dynamics to the system, the OHTC is calculated from the relation shown in Table 2. Different values of OHTC may be one reason for the different reactor dynamics. Henderson's correlation may be preferred to calculate the dynamics of the PMMA reactors. The experimental work to compare this model will be shown in a forthcoming paper.

NOMENCLATURE

A_r : total heat transfer area
C_i : concentration of species i
C_{pi} : heat capacity of species i
$(-\Delta H_r)$: heat of reaction
I : initiation concentration
k_d : rate constant for initiation
k_p : rate constant for propagation
k_t : rate constant for termination
M : monomer concentration
Pr : Prandtl number
q_{cf} : coolant feed rate
Re : Reynolds number
S : solvent concentration
$\Delta\tilde{S}_p^o$: entropy change accompanying polymerization at standard state
T : reaction temperature
T_{ad} : adiabatic temperature
T_c : coolant temperature
T_{ce} : ceiling temperature
T_{cf} : coolant feed temperature
T_{cr} : critical reaction temperature
T_f : feed temperature
T_{gi} : glass transition temperature, i=M, p, s
T_x : temperature under no reaction
t : time
U : overall heat transfer coefficient
U_0 : overall heat transfer coefficient at zero conversion
V : reactor volume
V_c : volume of a cooling jacket
V_{fi} : fraction free volume, i=M, p, s
V_{ref} : reference free volume
X_1 : dimensionless monomer concentration
X_2 : dimensionless initiator concentration
X_3 : dimensionless temperature
X_4 : dimensionless solvent concentration
X_5 : dimensionless polymer concentration

Greek Letters

θ : dimensionless residence time
η : the ratio of initiation feed concentration to monomer feed concentration
η_m : viscosity of monomer
η_p : viscosity of medium
ϕ_i : volume fraction of species i, M, p, s
ρ_i : density of species i

Subscripts

c : coolant
d, I : initiator
f, F : feed
M, m : monomer
o : initial
p : polymer
ref : reference
S, s : solvent
t : termination

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