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# NONISOTHERMAL REACTORS

## THEORY AND APPLICATION OF THERMAL TIME DISTRIBUTIONS

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**Abstract**—For reactions in nonisothermal systems, the thermal time distribution is the analog of the residence time distribution If the reaction can be characterized by a single activation energy, knowledge of the thermal time distribution based on this activation energy can be used to predict the yield of a first order reaction uniquely and to closely bound the yield for reactions of order other than first

Thermal time distributions are a useful conceptual and analytical tool for reaction engineering, particularly in systems where the temperature and velocity profiles are not strongly coupled to the extent of reaction This situation frequently occurs in the processing of polymer melts, for example in the activation of blowing agents or in chemical modification of the polymer chain Simplified flow models of heat exchange and extrusion equipment are used to illustrate the application of thermal time distributions and to show that they often differ significantly from the residence time distribution in the same device In fixed wall heat exchangers, the thermal time distribution shows less uniform reaction conditions than would be true for an isothermal reaction governed by the residence time distribution In extruders, and particularly for those where viscous dissipation is the major energy input, this situation is dramatically reversed with a reaction environment very similar to that for piston flow and substantially better than would occur in the same equipment operated isothermally

### INTRODUCTION

The theory of residence time distributions has well established and broad applications in the field of chemical reaction engineering This is true despite limitation of the theory to homogeneous reactions in isothermal systems For such cases, knowledge of the RTD is sufficient to predict the yield of a first order reaction uniquely and to closely bound the yield for reactions of order other than first[1, 2] Although there are situations where a more precise characterization of mixing phenomena is needed to understand the system, the RTD still represents a necessary starting point for analysis Indeed, it is fair to say that knowledge of the RTD is the most important step in reactor analysis beyond knowledge of the batch kinetics themselves

However, for reactors which are not homogeneous and isothermal, the RTD becomes much less useful and may even prove misleading if improperly applied One approach to these more complex systems is the theory of generalized time distributions which is outlined in Appendix A For the case of an isothermal, homogeneous reaction, the generalized time is just the time spent in the reactor, and thus the generalized theory reduces to classical RTD theory If the reaction is homogeneous but nonisothermal, the pertinent generalized time is the thermal time

### THERMAL TIME DISTRIBUTIONS

The theory of thermal time distributions can be developed along lines very similar to those used by Zwietering[1] in his treatment of residence time distributions In this theory, a molecule has three time-based attributes a residence age $\alpha$, a residence life expectancy $\lambda$, and a residence time $t$ These are related by

$$t = \alpha + \lambda \tag{1}$$

Zwietering considered the kinds of mixing that could occur between molecules of differing residence age, such mixing always being subject to the restriction of a constant residence time distribution He showed that molecules can mix only if they have the same life expectancy and that there are two extreme possibilities for such mixing complete segregation and maximum mixedness

In a completely segregated reactor, there is no mixing at all between molecules of differing residence age Molecules which enter together remain together and mix with other molecules only at the reactor exit Such a system can be modeled as a piston flow reactor with a number of side exits All fluid enters at a common point and flows down the reactor without mixing Fluid leaves from the reactor through the side exits, the number and placement of these exits being arranged to give the system the overall residence time frequency function $f(t)$ Mixing between molecules with differing $\alpha$ occurs only when $\alpha = t$ and $\lambda = 0$ Thus such mixing is said to be as late as possible Axial position down the reactor can be characterized by the value of $\alpha$ which ranges from $\alpha = 0$ at the extrance to $\alpha = t_{\max}$ at the downstream end The concentration profile in this isothermal reactor is governed by

$$\frac{dc}{d\alpha} = -kG(c) \tag{2}$$

subject ot the condition that $c = C_0$ at $\alpha = 0$ The solution to eqn (2) is identical to that for a batch reactor The exit concentration is obtained by averaging over the various side exits

$$\frac{\bar{c}}{c_0} = \int_0^\infty [c(t)]_{\text{batch}} f(t)\,dt \tag{3}$$

Zwiertering showed that the other extreme of micromixing can be modeled as a piston flow reactor with a number of side entrances Similarly to the exits in the segregated case, the side entrances are arranged to give residence time frequency function $f(t)$ Now, however, entering molecules with residence age $\alpha = 0$ are mixed with molecules already in the reactor with quite different ages Once mixed, the molecules will all exit together and at the point of mixing all have a common value of $\lambda$ Axial position in the piston flow reactor is characterized by the value of $\lambda$ which varies from $\lambda = 0$ at the exit to $\lambda = t_{\max}$ at the upstream end In the maximum mixedness reactor, mixing between molecules with different values of $\alpha$ occurs as early as possible Indeed, some of the molecules mixed will have $\alpha = 0$ and thus $\lambda = t$ while in the segregated reactor mixing occurs only when $\alpha = t$ and $\lambda = 0$ The composition profile down the reactor is governed by

$$\frac{dc}{d\lambda} = -kG(c) + \frac{f(\lambda)(c - c_0)}{1 - F(\lambda)} \tag{4}$$

subject to the condition that $c$ is bounded for all $\lambda$ The average exit concentration is found by evaluating the solution of (4) at $\lambda = 0$

Having restated the basic results of RTD theory for isothermal reactors, it is now possible to develop the analogous theory for non-isothermal reactors We begin by defining three temperature and time-based attributes of a molecule the thermal age $\alpha_T$, the thermal life expectancy $\lambda_T$, and the thermal time $t_T$ The defining equations are

$$\alpha_T = \int_0^\alpha e^{-E/RT(t')}\,dt' \tag{5}$$

$$\lambda_T = \int_\alpha^t e^{-E/RT(t')}\,dt' \tag{6}$$

and

$$t_T = \int_0^t e^{-E/RT(t')}\,dt' \tag{7}$$

In these equations, the temperature experienced by each molecule is considered to be function of the time that the molecule has spent in the reactor Physically, eqns (5)–(7) represent integrals taken along various portions of a fluid streamline It is apparent that $\alpha_T$, $\lambda_T$ and $t_T$ all have dimensions of time and are related by

$$\alpha_T + \lambda_T = t_T \tag{8}$$

The physical significance of the Arrhenius temperature dependency in eqns (5)–(7) springs from the assumed form of the rate equation for the nonisothermal reaction

$$\text{Rate} = k_0\, e^{-E/RT} G(c) \tag{9}$$

We will return to this physical interpretation shortly, but for the moment will develop the theory of mixing in nonisothermal systems without reference to reaction kinetics

Considering all molecules which enter or leave the reactor, define the thermal time frequency function as

$$h(t_T)\,dt_T = \text{Fraction of molecules with a thermal time between } t_T \text{ and } t_T + dt_T \tag{10}$$

The mean, $\bar{t}_T$ and higher moments of the thermal time distribution are defined in the usual way

$$\mu_n = \int_0^\infty (t_T)^n h(t_T)\,dt_T \tag{11}$$

where $\mu_0 = 1$ and $\mu_1 = \bar{t}_T$ We also define the cumulative distribution function as

$$H(t_T) = \int_0^{t_T} h(t_T')\,dt_T' \tag{12}$$

The existance of the distribution functions and of $\bar{t}_T$ follows from the existance of $f(t)$ and the mean residence time $\bar{t}$ To see this, note that there will be some minimum and maximum tempreatures within the reactor and corresponding minimum and maximum Arrhenius factors

$$\Psi_{\min} = e^{-(E/RT_{\min})}, \qquad \Psi_{\max} = e^{-(E/RT_{\max})} \tag{13}$$

Thus for each molecule,

$$\Psi_{\min} t \le t_T \le \Psi_{\max} t \tag{14}$$

If the entire reactor operated isothermally at $T_{\min}$, the distribution of thermal times would be identical to the distribution of residence times except for a constant factor

$$h(t_T) = \frac{1}{\Psi_{\min}} f(t_T/\Psi_{\min}) \tag{15}$$

A similar relation holds at $T_{\max}$ and thus we have

$$\Psi_{\min} \bar{t} \le \bar{t}_T \le \Psi_{\max} \bar{t} \tag{16}$$

For nonisothermal operation, $\bar{t}_T$ will differ from $\bar{t}$ as will $h(t_T)$ from $f(t)$ It is useful to define a system average Arrhenius factor by

$$\Psi = \bar{t}_T / \bar{t} \tag{17}$$

which corresponds to a special kind of system average temperature For every nonisothermal reactor, one can devise an equivalent isothermal reactor, operating at this average temperature By equivalence we mean only that

$$\Psi h(t_T) = f(t) \tag{18}$$

but we shall subsequently show that the two reactors are also equivalent in that they have the same bounds on micromixing

Now consider the kinds of mixing that can occur between molecules of differing thermal age If a constant thermal time distribution is to be maintained, molecules can mix only if they have the same value of thermal life expectancy Consider two groups of molecules with the same value of $\lambda_T$ but different values of $\alpha_T$ and hence of $t_T$ One possibility is that they mix only when $\lambda_T = 0$ which is at the reactor exit Such mixing occurs as late as possible Another extreme is for the mixing to occur when the younger of the two groups enters the reactor, i e when $\alpha_T = 0$ for one group and $\alpha_T > 0$ for the other Such mixing occurs as early as possible If $t_T$ is the thermal time for the younger of the groups, they can mix when $\lambda_T$ has any value within the range $0 \le \lambda_T \le t_T$

If all mixing between molecules with differing thermal ages occurs when $\lambda_T = 0$, the system is said to be completely segregated with respect to thermal ages If it occurs when $\alpha_T = 0$, the system is said to be in the state of maximum mixedness with respect to thermal ages These two conditions represent bounds on the level of micromixing (with respect to thermal ages) which is possible in a real reactor with fixed $h(t_T)$ In the isothermal case, Zwietering supposed that the bounds on micromixing provided bounds on reaction yield We make the same supposition for nonisothermal reactors It is also possible to apply the recent proof and conditions of Chauhan, Bell and Adler[2] directly to nonisothermal reactors This is discussed in Appendix B

At this point it remains to develop models and yield expressions for reactors operating at the two extremes of micromixing with respect to thermal ages These models follow directly from the models used by Zwietering and from the concept of equivalent reactor For the segregated case the model reactor is a piston flow reactor with many side exits It is operated isothermally at the temperature defined by eqn (17) and with the side exits arranged to give $f(t)$ as defined by eqn (18) In this model, $t_T = \Psi t$ with $\Psi$ constant The concentration profile is given by the batch reaction kinetics

$$\frac{dc}{d\alpha} = k_0 \Psi G(c) \tag{19}$$

or, substituting for $\alpha$

$$\frac{dc}{d\alpha_T} = -k_0 G(c) \tag{20}$$

The average exit concentration is given by

$$\frac{\bar{c}}{c_0} = \int_0^\infty [C(t_T)]_{\mathrm{batch}} h(t_T)\, dt_T \tag{21}$$

Similarly to the above, the maximum mixedness reactor is isothermal and piston flow but now side entrances are used to duplicate $f(t) = 1/\Psi h(t_T)$ The concentration profile is governed by

$$\frac{dc}{d\lambda_T} = -k_0 G(c) + \frac{h(\lambda_T)(c - c_0)}{1 - H(\lambda_T)} \tag{22}$$

subject to the condition that $c$ is bounded for all $\lambda_T$ This condition usually can be restated as

$$\lim_{\lambda_T \to \infty} \frac{dc}{d\lambda_T} = 0 \tag{23}$$

The exit concentration is the solution to eqn (22) evaluated at $\lambda_T = 0$

The model reactors have residence time distributions with the same functional form as the thermal time distribution of the real reactor We note in passing that the real reactor will also have a residence time distribution but this in general will be different from that of the model reactors Molecules with the same value for $\lambda_T$ may have different values for $\lambda$ Thus the kinds of mixing possible with a constant $h(t_T)$ may not be possible with a constant $f(t)$ and conversely Similarly, reactors is an extreme state of micromixing with respect to thermal ages need not be in an extreme state of micromixing with respect to residence ages In particular, one can devise systems which are completely segregated with respect to thermal ages but not so with respect to residence ages and conversely

## DETERMINATION OF $h(t_T)$

Residence time distributions are determined in two main ways

(1) Experimentally by inert tracer techniques

(2) Theoretically by means of flow models

Turning to thermal time distributions, there is no simple experimental method for determining them, a fact that severely limits their usefulness However, theoretical determinations based on a combined thermal and flow model are possible These will tend to be specific for a particular reaction system if the flow patterns or temperature profiles are strongly coupled to the extent of reaction, but even here the thermal time distribution is a useful conceptual tool for explanation and analysis of reactor phenomena It becomes significantly more useful for that class of problems where the extent of reaction does not significantly affect the equations of motion or energy

The field of polymer reaction engineering includes examples of both situations Polymerizations and particularly bulk polymerizations usually show a dramatic influence of the extent of reaction on temperature and velocity profiles Here the thermal time distribution—like the residence time distribution—will be system specific and useful only in an interpretative mode On the other hand, the processing of polymers in extruders, heat exchangers, and fabrication equipment often involves chemical reactions which have relatively little influence on the temperature and flow patterns Industrially important examples include the modification of polymer end-groups and side chains, thermal depolymerization, and the activation of chemical blowing agents It is usually true for such systems that the fluid is in steady, laminar flow so that the equations of motion and energy are comparatively easy to solve Further, the deterministic nature of the solutions assures that the functions $f(t)$ and $h(t_T)$ are themselves deterministic and can be calculated directly The following sections will illustrate these calculations for some simplified thermal and flow models of polymer processing equipment

## LAMINAR FLOW HEAT EXCHANGERS

Figure 1 illustrates the system to be considered and indicates the nomenclature The important simplifying assumption is that there is only one significant velocity component, $V_z(y)$ The geometry of the heat exchanger determines the specific choice of a coordinate system and the exact nature of the solutions However, results will be qualitatively similar for all situations involving heat transfer to fluids in laminar flow with an axisymmetric velocity profile which is independent of distance down the exchanger It is supposed that the flow problem has been solved so that $V_z(y)$ is known Then the heat transfer and temperature history aspects of the problem are defined by three dimensionless groups

$$\frac{aL}{\bar{V}B^2},\ \frac{T_w}{T_0},\ \frac{E}{RT_0} \tag{24}$$

The first of these is a form of the Graetz Number, and if this is large enough, the thermal time becomes just a constant multiple of the residence time For smaller $Gz$, temperature gradients in the $y$-direction become important, and the $H_T$ must be calculated by integrating along the streamlines according to eqn (7)

As a specific example, we treat a parallel plate heat exchanger with Newtonian velocity profile

$$V_z(y) = 1\ 5\,\bar{V}(1 - y^2/B^2) \tag{25}$$

The temperature profiles are calculated as functions of $Gz$ and $T_w/T_0$, and $t_T$ is calculated by integration down the length of the exchanger

$$t_T(y) = \int_0^L e^{-(E/RT(z\ y))} \frac{dz}{V_z(y)} \tag{26}$$

which yields $t_T$ as a function of $y$ Assuming that $t_T$ is monotonic in $y$, the distribution function $H$ can be found as a function of $y$

$$H(y) = \int_0^L V_z M\,dy \tag{27}$$

Where $M = 1/L$ for flow between flat plates and $M = 2y/B^2$ for flow in a circular pipe The parameter $y$ can be eliminated between eqns (26) and (27) so that $H$ is obtained as a function of $t_T$ Representative results are shown in Fig 2 where, for ease of comparison, all the distribution functions have been scaled to have unit mean

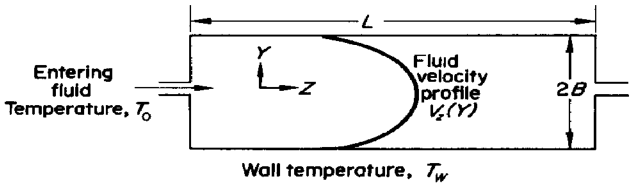

Fig 1 Laminar flow heat exchanger

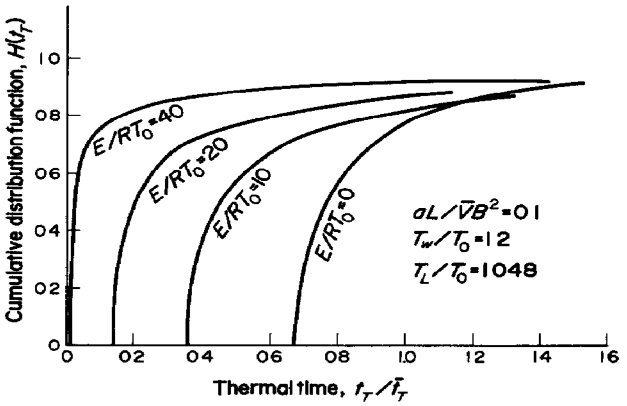

Fig 2 Thermal time distributions for parallel plate heat exchanger

This point is perhaps worth emphasizing since it is far from obvious based on the graphical representations in Fig 2 The various distribution functions differ dramatically in the tail region, and those corresponding to high activation energies show a phenomenon akin to bypassing Only the material near the wall makes a significant contribution to the mean thermal time, $\bar{t}_T$, while material near the center of the flow channel leaves the system with a very low value of $t_T$ Appendix C describes the numerical technique used to evaluate $\bar{t}_T$

The curve marked $E/RT_0 = 0$ in Fig 2 is identical to the residence time distribution This same distribution function also arises for the other limiting case of $aL/\bar{V}B^2 = 0$ or $T_W/T_0 = 1$ For Newtonian flow between parallel plates, this function is

$$F(t) = 0, \qquad 0 < t < 2/3\bar{t} \tag{28}$$

$$F(t) = (1 + \bar{t}/3t)\sqrt{(1 - 2\bar{t}/3t)}, \quad t > 2/3\bar{t}$$

## SINGLE SCREW MELT EXTRUDER

This section treats a simplified thermal and flow model of the single-screw melt extruder The flow model is assumed to be independent of the thermal model, and in treating it, we will closely follow the work of Pinto and Tadmor[3] who derived the RTD for this model Figure 3 illustrates the geometry and indicates the notation There are two velocity components $V_z(y)$ which represents flow down the channel and $V_x(y)$ which represents a circulatory pattern in the $x$-$y$ plane It is assumed that the channel width, $W$, is large compared to the height, $H$, so that the $y$-direction velocity components at each end of the channel will have a negligible effect on residence time and heat transfer characteristics

For a Newtonian fluid with constant viscosity, the

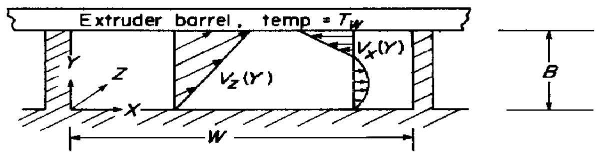

Fig 3 Flow channel in a single screw extruder

circulatory velocity component is

$$V_x(y) = V_0(y/B)(2 - y/B)\cos\theta \tag{29}$$

Fluid moves in the negative $x$-direction while it is in the upper third of the channel and in the positive $x$-direction while in the lower two thirds, and a fluid element which first crosses the channel at position $y$ will later recross it at position $y_c$, these two coordinates being related by

$$Y_c = 1/2[1 - Y + \sqrt{(1 + 2Y - 3Y^2)}] \tag{30}$$

where $Y = y/B$. For the velocity component in the $z$ direction we use

$$V_z(y) = V_0(y/B)\sin\theta \tag{31}$$

which assumes that the extruder operates with an open discharge (no back pressure). The combination of the two velocity profiles means that the fluid follows a helical path down the extruder channel, and eqn (7) is evaluated by integrating along these helical streamlines.

Thermal aspects of the problem are governed by the differential equation

$$V_x\frac{\partial T}{\partial x} + V_z\frac{\partial T}{\partial z} = a\frac{\partial^2 T}{\partial y^2} \tag{32}$$

where conduction in the two dimensions parallel to the velocity components has been neglected. More importantly, eqn (32) ignores viscous dissipation although this restriction will later be removed since viscous dissipation is the major source of heat input for most extrusion operations. Also, the viscosity of the melt is usually dependent on temperature and shear rates, but these real effects are neglected since the current emphasis is on illustrating general concepts rather than on construction of a rigorous model of the extrusion process.

Heat conduction through the barrel wall is approximated by a constant wall temperature, $T = T_w$ at $y = B$. A neutral screw is assumed so that a zero flux condition is applied at $y = 0$. The boundary conditions at $x = 0$ and $x = W$ reflect circulation of fluid in the $x - y$ plane

$$\begin{aligned} T(0, y) &= T(0, y_c) \\ T(W, y_c) &= T(W, y) \end{aligned} \tag{33}$$

where $y$ and $y_c$ are related through eqn (30).

Using these boundary conditions, eqn (32) can be solved for the three-dimensional temperature profile using standard numerical techniques. A convenient approach is a finite difference approximation with a grid spacing in the $y$-direction based on eqn (30). Thus one might choose equally spaced grid points in the region $2/3 < Y < 1$ and then use eqn (30) to calculate the points for the region $0 < Y < 2/3$.

The solution of eqn (32) depends on three dimensionless groups

$$\frac{aL}{V_0B^2\sin\theta}, \quad \frac{L\cos\theta}{W\sin\theta}, \quad \frac{T_w}{T_0} \tag{34}$$

The first of these is a form of the Graetz Number and the second is an aspect ratio. Figure 4 shows a typical temperature profile at the discharge end of the channel. Note the expanded scale used in the plot. The exit temperature distribution is actually quite uniform. Suppose $T_w/T_0 = 1.2$ corresponds to an inlet temperature difference of 100°C. Then the maximum temperature difference between any two points in the exit stream would be 17°C.

With known temperature profiles, $t_T$ is found by integrating along a streamline according to eqn (7). Exact specification of the streamlines requires knowledge of the initial values for both $x$ and $y$. However, the effect of the initial $x$ coordinate becomes unimportant in long channels, and, as in the RTD analysis of single screw extruders[3], we neglect the effect of initial $x$. Then the streamline integral in eqn (7) can be expressed as

$$\begin{aligned} t_T(y) = {} & \phi\int_0^L\int_0^W e^{-(E/RT)}\frac{dx}{W}\frac{dy}{V_z(y)} \\ & + (1-\phi)\int_0^L\int_0^W e^{-(E/RT)}\frac{dx}{W}\frac{dy_c}{V_z(Y_c)} \end{aligned} \tag{35}$$

where $2B/3 < y < B$ and where $\phi$ is the fraction of the volumetric flow rate passing through a differential element, $dy$, in the upper third of the channel compared to the total flow through differential elements, $dy$ and $dy_c$ in both portions of the channel. Thus,

$$\begin{aligned} \phi &= \frac{1}{1 + \dfrac{V_z(Y_c)}{V_z(Y)}\left|\dfrac{dY_c}{dy}\right|} \\ &= \frac{1}{1 + \dfrac{Y_c}{2Y}\left[1 + \dfrac{(3Y-1)}{\sqrt{(1+2Y-3Y_2)}}\right]} \end{aligned} \tag{36}$$

Note that $\phi$ is a fraction based on volumetric flow rates and is thus different than the fractions based on velocities which were defined by Pinto and Tadmor[3]. Practical evaluation of $t_T$ means that one first averages across the channel and then integrates in the downstream direction. This is done separately for the upper and lower portions

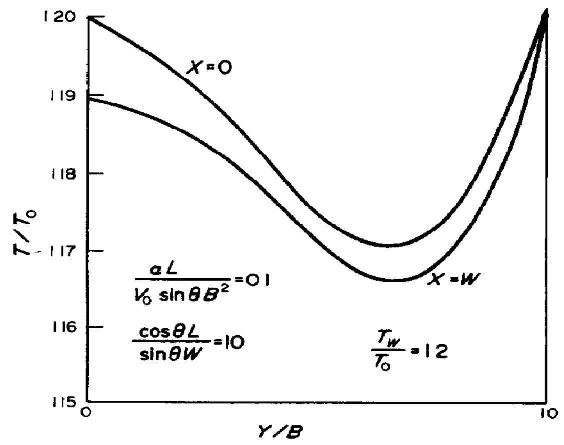

Fig. 4. Temperature profile in extruder channel.

of the channel and the results are combined according to eqn (35) This gives $t_T$ as a function of $y$ Pinto and Tadmor's result for $F(y)$ can be directly applied to give $H$ as a function of $y$

$$H(y)=1/2[2Y^2-1+(Y-1)\sqrt{(1+2Y-3Y^2)}] \tag{37}$$

The parameter $y$ is then eliminated to give $H$ as a function of $t_T$ Typical results, scaled so that $\bar{t}_T=1$, are given in Fig 5 Appendix C describes the numerical technique used to obtain $\bar{t}_T$

The curve for $E/RT_0=0$ is the same as the residence time distribution, and, like the RTD, gives $(t_T)_{\min}=0\ 75\ \bar{t}_T$ For $E/RT_0$ up to about 10, the value for $(t_T)_{\min}$ is higher for that for the RTD Thus with activation energies in this range, the model suggests a more uniform reaction environment than if the extruder were operated isothermally This perhaps surprising result is due to a compensatory coupling between temperature and residence time where the fluid elements with shorter residence times tend to experience higher temperatures In the fixed-wall, laminar-flow heat exchanger considered earlier, the opposite coupling occurs and $H(t_T)$ shows much greater deviations from the ditribution corresponding to plug flow than does $F(t)$

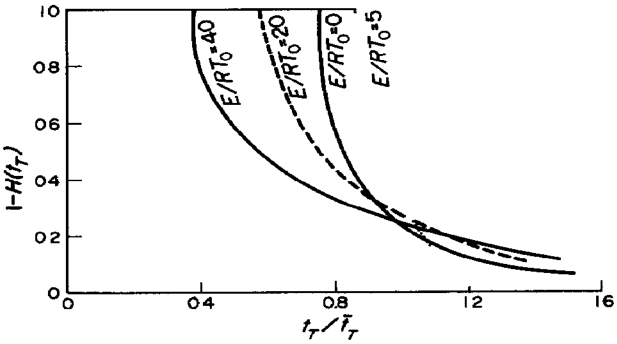

Fig 5 Thermal time distributions in a single screw extruder

### EXTRUDER WITH VISCOUS DISSIPATION

Viscous dissipation is an important phenomenon in most extrusion operations Indeed, it is usually the major and sometimes the sole source of energy input To account for this, we must add the appropriate source terms to the energy equation

$$V_x\frac{\partial T}{\partial x}+V_z\frac{\partial T}{\partial z}=\alpha\frac{\partial^2 T}{\partial y^2}+\frac{2\mu}{\rho c_v}\left[\left(\frac{\partial V_z}{\partial y}\right)^2+\left(\frac{\partial V_x}{\partial y}\right)^2\right] \tag{38}$$

where $V_x$ and $V_z$ are the same as used by Pinto and Tadmor[3] and are given by eqns (29) and (31) Reducing eqn (38) to dimensionless form gives rise to two very similar versions of the Brinkman Number

$$\frac{\mu V_0^2\sin^2\theta}{\kappa T_0},\quad \frac{\mu V_0^2\cos^2\theta}{\kappa T_0} \tag{39}$$

The solution to eqn (38) also depends on the same dimensionless groups and boundary conditions as for eqn (32) Figure 6 gives sample results for a case where a zero-flux condition was applied at both the screw root ($y=0$) and at the barrel surface ($y=B$) Physically, this example might correspond to heating a polymer melt by 100°C Then the exit temperature distribution is even more uniform than in the wall conduction case treated earlier. The maximum temperature difference in the exit stream is only 11°C, and this temperature difference is in fact the maximum one that occurs anywhere down the extruder With heat transfer through the barrel, the maximum exit temperature difference is 17°C while fluid elements near the inlet of the extruder will show a temperature difference up to 100°C

Figure 7 shows the thermal time distributions resulting from the viscous heating example The curve for $E/RT_0=0$ is identical to that in Fig 5 and is the same as the residence time distribution The other curves show that low residence times are coupled with higher temperatures to a remarkable extent For $E/RT_0=5$, $(t_T)_{\min}=0\ 98$ and $H(t_T)$ is practically indistinguishable from that of a piston flow reactor For all values of $E/RT_0$, $(t_T)_{\min}$ lies in the range 0 75–1 0 Thus for all activation energies, one can expect a more uniform reaction environment in an extruder with viscous heating than in the same equipment operated isothermally

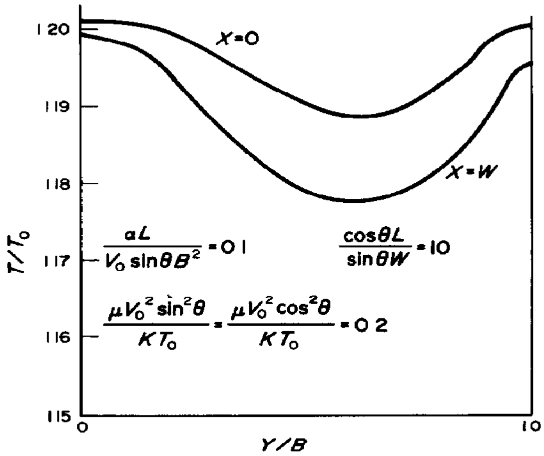

Fig 6 Extruder temperature profile with viscous dissipation and insulated walls

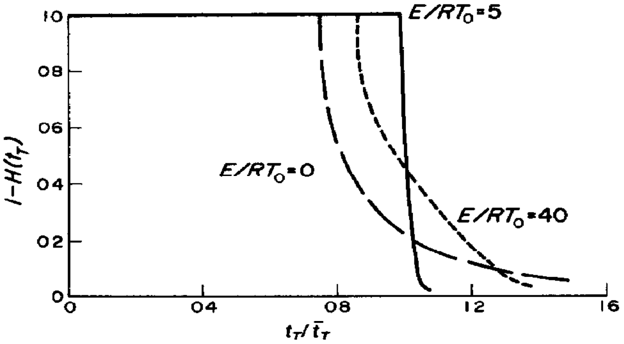

Fig 7 Thermal time in an extruder with viscous dissipation

## CONCLUSIONS

We have introduced the concept of thermal time distributions in nonisothermal reactors This is a unifying concept which allows nonisothermal systems to be treated within the theoretical framework previously used for isothermal systems

From a predictive viewpoint, thermal time distributions are most useful in systems where the temperature and velocity profiles are independent of the extent of reaction Thus one may calculate the thermal time distribution from a thermal and flow model of the system and then use the calculated results to bound the reaction yield in exactly the same way that the residence time distribution can be used to bound the yield of an isothermal reaction

The sample calculations provide useful insight into the design of laminar flow reactors with conduction through the wall of a fixed-wall heat exchanger Long residence times are coupled to relatively high temperatures The result is a thermal time distribution grossly different from that of piston flow or even the residence time distribution in the same device However, in moving-wall devices such as single screw extruders, it is possible to reverse this coupling at least partially so that fluid elements with higher temperatures have lower residence times The circulatory flow pattern within the screw channel also acts to improve uniformity The overall result is that reactor performance is greatly improved compared to fixed-wall devices Depending on the activation energy, the thermal time distribution is roughly similar to the residence time distribution in the same equipment For extruders with thermal input from viscous dissipation rather than heat conduction through the barrel, the thermal environment is still more uniform Within a range of activation energies, the thermal time distribution may be virtually identical to the piston flow distribution, and for any activation energy, the thermal time distribution represents a more uniform reaction environment than the residence time distribution

## NOTATION

| | |
|---|---|
| $a$ | thermal diffusivity |
| $B$ | channel height or half height |
| $c, c_a, c_b$ | concentration |
| $C_v$ | heat capacity |
| $E$ | activation energy |
| $f$ | residence time frequency function |
| $F$ | residence time distribution function |
| $G$ | concentration function |
| $h$ | thermal time frequency function |
| $H$ | thermal time distribution function |
| $k, k_0$ | constants in rate equation |
| $K$ | function of reaction parameters |
| $L$ | length of channel |
| $P_1, P_2$ | reaction parameters |
| $Q$ | volumetric flow rate |
| $r$ | reaction rate function |
| $R$ | gas law constant |
| $t$ | residence time |
| $t_G$ | generalized time |
| $t_T$ | thermal time |
| $T$ | absolute temperature |
| $T_0$ | inlet temperature |
| $T_W$ | wall temperature |
| $V$ | fluid velocity |
| $V_0$ | velocity at barrel surface, $\pi DN$ |
| $W$ | width of channel |
| $x$ | coordinate |
| $y$ | coordinate |
| $y_c$ | defined by eqn (14) |
| $Y$ | dimensionless coordinate, $y/B$ |
| $z$ | coordinate |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | residence age |
| $\alpha_G$ | generalized age |
| $\alpha_T$ | thermal age |
| $\epsilon$ | mixing time in isothermal systems |
| $\epsilon_T$ | mixing time in nonisothermal systems |
| $\lambda$ | residence life expectancy |
| $\lambda_G$ | generalized life expectancy |
| $\lambda_T$ | thermal life expectancy |
| $\theta$ | helex angle of screw extruder |
| $\kappa$ | thermal conductivity |
| $\mu$ | viscosity |
| $\Psi$ | Arrhenius factor |
| $\tau$ | ratio of thermal time to residence time |
| $\phi$ | fraction defined by eqn (18) |

## REFERENCES

[1] Zwietering T N , *Chem Engng Sci* 1959 **11** 1
[2] Chauhan S P , Bell J P and Adler R J , *Chem Engng Sci* 1972 27 585
[3] Pinto G and Tadmor Z , *Poly Engng Sci* 1970 **10** 279
[4] Nauman E B and Collinge C N , *Chem Engng Sci* 1968 **23** 1309, 1317
[5] Danckwerts P V , *Chem Engng Sci* 1953 **2** 1
[6] Orcutt J C , Davidson J F and Pigford R L , *Chem Engng Prog Symp Series* 1962 **58** 1

## APPENDIX A

### *Theory of generalized time distributions*

Consider a reaction with rate equation

$$\text{Rate} = r(c_A, c_B, \quad , P_1, P_2, \quad ) \tag{40}$$

where $c_A, c_B,$ represent concentrations of the various molecular species involved in the reaction and where the $P_1, P_2,$ are all those reaction parameters, other than concentration, which vary from point to point in the system These include such factors as temperature, catalyst density, radiation intensity, etc as may be appropriate for the particular system Following an earlier work[4] we suppose that $r$ can be factored to give

$$\text{Rate} = k_0 K(P_1, P_2, \quad ) G(c_A, c_B, \quad ) \tag{41}$$

so that $K$ depends only on the $P$, $G$ depends only on the $c$, and $k_0$ is system constant included for convenience

For each molecule in the reactor we define three attributes a generalized age $\alpha_G$, a generalized life expectancy $\lambda_G$, and a generalized time $t_G$ The defining equations are

$$\alpha_G = \int_0^\alpha K(t')\,dt' \tag{42}$$

$$\lambda_G = \int_\alpha^t K(t')\,dt' \tag{43}$$

$$t_G = \int_0^t K(t')\,dt' \tag{44}$$

and it follows that

$$\alpha_G + \lambda_G = t_G \tag{45}$$

Considering all molecules as they leave the system, the generalized time function is defined by

$h(t_G)\,\mathrm{d}t_G$ = Fraction of molecules with a generalized time between $t_G$ and $t_G + \mathrm{d}t_G$

From a theoretical viewpoint, it is not necessary that $h(t_G)$ be regarded as deterministic in nature It will be deterministic if, for example, the parameters $P$ are fixed functions of the spatial coordinates and if the fluid is in laminar flow For turbulent flow it may be more useful to consider $h(t_G)$ as a probability distribution

With the above definitions, it is possible to develop the theory in a manner essentially indentical to that for thermal time distributions Micromixing is characterized by the earliness or lateness of mixing between molecules with different generalized reaction ages If the mixing is done as late as possible, i e when $\lambda_G = 0$, the system is said to be completely segregated with respect to generalized ages The model reactor operates at a suitably average value for $K$ so that $f(t)$ has the same functional form as $h(t_G)$ The concentration profile down the reactor is given by

$$\frac{\mathrm{d}c}{\mathrm{d}\alpha} = -K_0 K(P_1, P_2, \quad) G(c_A, c_B, \quad) \tag{46}$$

or, substituting for $\alpha$,

$$\frac{\mathrm{d}c}{\mathrm{d}\alpha_G} = -K_0 G(c_A, c_B, \quad) \tag{47}$$

The analog of eqn (21) follows directly, the only difference being that $t_T$ is replaced by $t_G$

When all mixing between molecules with differing $\alpha_G$ is done as early as possible, i e when $\alpha_G = 0$ for the youngest molecule, the system is in maximum mixedness A Zwietering type differential equation can be derived for the model reactor The result is simply eqn (22) with $\lambda_G$ substituted for $\lambda_T$

The two extremes of micromixing normally provide bounds on the yield of a reaction The proof of this statement and necessary conditions are discussed in Appendix B, the extension from thermal times to generalized times being obvious

It is seen from the above that the generalized time distribution is a generalization of the residence time distribution which allows complex reaction systems to be treated within the same theoretical framework used for isothermal, homogeneous reactions From a theroetical viewpoint, applicability of this theory rests on the assumed separability of variables according to eqn (41) From a practical viewpoint, difficulties in determining $h(t_G)$ represent a more serious obstacle although these are gradually being overcome Table 1 summarizes applications to date

## APPENDIX B

### *Optimum micromixing in nonisothermal reactors*

In this Appendix we apply the theory of Chauhan, Bell and Adler[2] to nonisothermal reactors They considered the mixing between two groups of molecules with the same residence life expectancy This mixing can occur at any time $\epsilon$ within the interval $0 \leq \epsilon \leq \lambda$ It was shown that the averaged concentration for the mixed group of molecules as they leave the reactor is a monotonic function of $\epsilon$ Conversion increases monotonically with increasing $\epsilon$ for concave-up rate expressions and decreases monotonically with increasing $\epsilon$ for concave-down rate expressions This conclusion applies to all groups of molecules which will be mixed within reactor and thus applies to the average conversion for the entire reactor

To apply the above approach to nonisothermal reactors, we begin with the batch rate equation

$$-\frac{\mathrm{d}c}{\mathrm{d}\alpha} = k_0\, e^{-E/RT} G(c) \tag{48}$$

Converting this to a rate based on thermal age rather than residence age gives

$$-\frac{\mathrm{d}c}{\mathrm{d}\alpha_T} = k_0 G(c) \tag{49}$$

Figure 8 illustrates the case where $G(c)$ is a concave-upward function of $c$ The points marked $A$ and $B$ represent the concentrations of two groups of molecules with the same value of $\lambda_T$ If they were mixed immediately, i e , at $\epsilon = 0$, the resultant average concentration, $c_M$, and average reaction rate are shown at point $M$ in Fig 8 The point $U$ represents the mathematically averaged concentration, $c_U$, and rate which results from leaving the two groups of molecules unmixed Since the reaction rate is concave-up, the rate is higher without mixing With a slight change in nomenclature, the analysis of Chauhan, Bell and Adler can be followed directly to prove

$$-\frac{\mathrm{d}c_U}{\mathrm{d}\alpha_T} > -\frac{\mathrm{d}c_M}{\mathrm{d}\alpha_T} \text{ for all } \alpha_T \geq 0 \tag{50}$$

so that $c_U$ decreases more rapidly with thermal age than $c_M$, for this concave-up example, the mixing time which maximizes conversion (minimizes concentration) for the two groups of molecules will be as late as possible, i e at $\lambda_T = 0$ which is complete segregation with respect to thermal ages

The argument is easily repeated for the concave-down case The

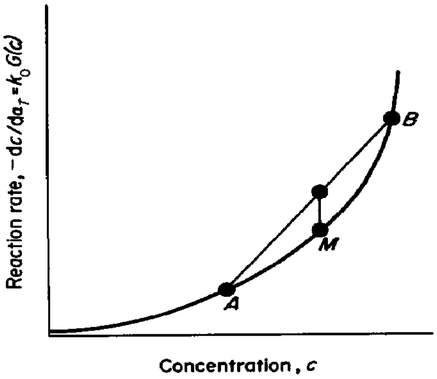

Fig 8 Concave-up reaction rate

Table 1 Examples of generalized time distributions

| Type of system | Type of distribution | Reference |
|---|---|---|
| Isothermal, Homogeneous | Residence time distribution | Dankwerts[5] |
| Isothermal, Heterogeneous | Contact time distribution | Orcutt *et al* [6]<br>Nauman and Collinge[4] |
| Non-isothermal, Homogeneous | Thermal time distribution | This paper |

result is that

$$-\frac{dc_M}{d\alpha_T} > -\frac{dc_U}{d\alpha_T} \quad \text{for all } \alpha_T \geq 0 \tag{51}$$

so that conversion is maximized with mixing as early as possible, i.e. at $\alpha_T = 0$ which is maximum mixedness with respect to thermal ages.

When the reaction rate is a linear function of concentration, $c_M = c_U$ and

$$-\frac{dc_M}{d\alpha_T} = -\frac{dc_U}{d\alpha_T} \quad \text{for all } \alpha_T \geq 0 \tag{52}$$

so that conversion is independent of the time of mixing. This is the classical result that the yield of a first order reaction is independent of micromixing.

## APPENDIX C

### *Numerical evaluation of* $\bar{t}_T$

A finite difference method for the numerical determination of thermal time distributions gives a value for $t_T$ at each of the interior grid points. Since $H$ can also be obtained at each of these points, it is possible to eliminate $y$ as a parameter and to evaluate $\bar{t}_T$ from its defining equation (eqn 11) or from similar forms such as

$$\bar{t}_T = \int_0^\infty [1 - H(t_T)]\, dt_T = \int_0^1 t_T(H)\, dH \tag{53}$$

The problem with such a direct method for determining $\bar{t}_T$ is that $t_T$ is unbounded over the internal of interest. Even with sophisticated numerical techniques, the difficulty in accurately integrating functions such as those in Fig. 2 will be readily appreciated.

To develop an alternate calculation technique for $\bar{t}_T$, note that

$$\bar{t}_T = \frac{1}{Q}\int_0^Q t_T\, dQ \tag{54}$$

where $\bar{t}_T$ remains unbounded but we have now converted to an integral over the volumetric flow rate. Now, the residence time $t$ is easily calculated for any position $y$

$$t = L/V_z(y) \tag{55}$$

We thus define the variable

$$\tau = t_T/t \tag{56}$$

and can evaluate its value at each of the interior grid points. We can also evaluate $\tau$ at the boundaries with the known boundary conditions, i.e. for constant wall temperature

$$\lim_{y \to \text{wall}} \tau = e^{-E/RT_W} \tag{57}$$

Thus $\tau$ is known for each grid point and is bounded for all $y$. Substituting into eqn (54) gives

$$\bar{t}_T = \frac{1}{Q}\int_0^Q \tau t\, dQ = \frac{1}{Q}\int_0^Q \frac{\tau L\, dQ}{V_z} \tag{58}$$

Now, for the parallel plate problem, $dQ = WV_z\, dy$ and

$$\bar{t}_T = \frac{1}{Q}\int_0^B \frac{\tau L}{V_z} WV_z\, dy = \frac{LW}{Q}\int_0^B \tau\, dy \tag{59}$$

Thus, evaluation of $\bar{t}_T$ merely requires integrating a bounded variable over a finite range. One simple method for doing this is to fit $\tau$ to a piecewise quadratic in $y_0$. For equally spaced mesh points, this is just Simpson's rule.

For geometries other than parallel plates the same general approach works although the specific form of eqn (59) will be altered. For a circular pipe, $dQ = 2\pi V_z\, dy$ and

$$\bar{t}_T = \frac{2\pi L}{Q}\int_0^B \tau y\, dy \tag{60}$$

which again has a bounded variable integrated over a finite range.

In the extruder problem, eqn (35) gives $t_T(y)$ with a collapsed range on $y$. Equation (58) remains valid, but $V_z$ and $dQ$ are now complicated functions of $y$ over the collapsed range $2/3 < y/B < 1$. A better approach is to leave $t_T$ in uncollapsed form by rewriting eqn (35) as

$$t_T(y) = \phi(t_T)_u + (1 - \phi)(t_T)_L \tag{61}$$

Then $\tau$ is defined in terms of $(t_T)_L$ for $0 < y/B < 2/3$ and in terms of $(t_T)_u$ for $2/3 \leq y/B < 1$. With this definition, eqn (59) stands as written, and $\bar{t}_T$ is readily calculated.