A Surface Renewal Model for the Drying of Polymers During Screw Extrusion

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Vacuum vented, single screw extruders are widely used by polymer processors to remove small amounts of volatile impurities from polymer melts. In a recent paper (3), Coughlin and Canevari presented the results of an experimental study of this devolatilization process. Two models were used to correlate the data, the first based on the assumption that volatile removal is limited by diffusion within the polymer melt, and the other based on the assumption that a mass transfer resistance at the polymer-gas interface is limiting. In these models, the creation of fresh surface caused by circulatory flow of polymer melt in the small cross section of the screw channel and by flow of polymer melt over the flights of the screw was neglected. Although both models correlated the experimental data well, the authors noted that the diffusion coefficient for the volatile material in the polymer melt, as calculated from the first model, was about four orders of magnitude too large. This suggests that neither model is based on a correct mechanistic interpretation of the drying process. The high calculated diffusivity also argues against the theory that heat transfer may limit the drying process.

The purpose of this paper is to explore, in an approximate fashion, the effect on the drying process of the renewal of exposed polymer surface in the extruder by the aforementioned mechanisms.

A SURFACE RENEWAL MODEL

Consider the screw channel cross section shown in Figure 1. Following normal practice, the curvature of the unwrapped channel is neglected. The situation to be described is most easily visualized if the reference frame is changed, and the screw is assumed to be stationary with the barrel moving. Let V_B be the x component (cross-channel component) of the barrel velocity, so that $V_B = \pi dN Sin\phi$. The polymer in contact with the barrel wall is also moving with an x component velocity of V_B. This motion has two important consequences that were neglected in reference 3. First, a circulatory flow is established in the x-y plane, as shown in Figure 1 (2). This flow causes a continuous renewal of the free surface at $x = 0$. Unfortunately, no quantitative treatment of this circulatory flow is presently available. It is therefore assumed that the y component of velocity at the free surface V_S is equal to V_B. Moffatt (8) has shown that the velocity of an infinite free surface perpendicular to a moving wall is $(2/\pi)$ times the wall velocity. The assumption that $V_B = V_S$ is therefore at least qualitatively reasonable.

Contrary to the assumption of the previous models, an element of polymer at the free surface remains exposed to vacuum for only a very short time, which is approximately given by $t_e = h/\pi dN Sin\phi$. For the data presented in reference 3, t_e has a maximum value of about 0.5 sec. Assuming that diffusion within the polymer limits the overall mass transfer process, and that the diffusion coefficient of volatile material in the polymer is about 10^{-4} in.^{2}/min., it can be calculated from existing solutions (4, 6) to the diffusion equation in a semi-infinite slab that the gradient in concentration of volatile material at the free surface is confined to a very thin layer, of the order of 0.002 in. The variation of V_y in the x direction at the free surface can therefore be neglected as a first approximation.

The model of the system now consists of a very thin element of polymer moving in the $+y$ direction along the free surface with a velocity V_B. Once this element reaches the barrel surface, the devolatilization process stops, and the element is either mixed into the bulk of the polymer, or more likely, is resaturated with volatile material by molecular diffusion from the bulk. In any event, it is assumed that each new element reaching point a in Figure 1 contains solvent at the same concentration C as the bulk of the polymer.

The total amount of solvent q_e removed from a unit area of polymer at the surface, in the time t_e, is given by the classical solutions for diffusion in a semi-infinite slab (6):

$$q_e = 2C\left(\frac{Dt_e}{\pi}\right)^{1/2} \qquad (1)$$

The total rate of solvent loss from the exposed polymer face is $q_e(dA/dt) = q_e V_B$ for a unit depth perpendicular to the cross section. This treatment is frequently referred to as the *penetration theory* in the chemical engineering literature. Note that the mass transfer resistance in the gas phase has been assumed to be negligible.

Coughlin and Canevari (3) and Latinen (5) have pointed out that there is also a second mechanism for evaporation of volatile material. From Figure 1, it can be seen that the barrel drags a thin film of polymer through the clearance between the screw flights and the barrel. It is reasonable to assume that Couette flow exists in this land area. Thus the velocity of the polymer is V_B at the barrel surface and decreases linearly to zero at the flight tip. Once the polymer passes the flight, the velocity gradient disappears and the velocity in all parts of the film is V_B. Continuity requires that the thickness of the film shrinks to half its original value once the polymer stream clears the flight. In the following analysis, it is assumed that the velocity gradient disappears, and the thickness of the film decreases to $\delta/2$, instantaneously, as soon as polymer passes the flight.

The polymer film coming over the flight is exposed to vacuum for a time t_f which is approximately given by

$$t_f = W(1 - f)/(\pi dN Sin\phi)$$

before it is mixed into the polymer in the upstream flight. For the data of the previous paper, t_f has a maximum value of about 1.3 sec. In this time, the concentration gradient penetrates to a depth of about 0.004 in., assuming that the diffusivity is about 10^{-4} in.^{2}/min. Since the land clearance in extruders is usually of the order of 3 to 10 mils, depending on the original design of the screw and on the amount of wear that has occurred, the semi-infinite slab approximation must be applied with caution, as it can over estimate the amount of volatile material that is removed.

The flow of polymer over the flights is at once both good and bad. On the positive side, it creates surface from which volatile material can evaporate. However, it also introduces a backmixing or axial dispersion effect which tends to reduce the efficiency of the devolatilization process.

To complete the formulation of the model, a steady state material balance on the volatile component is taken over a differential element of volume of thickness dz. The polymer is assumed to be in plug flow in the z direction. Let $C(z)$ be the concentration of the volatile component at some point z. Then: (Rate of component in across surface at $z = z$) + (Rate in over downstream flight) − (Rate out across surface at $z = z + dz$) − (Rate of vaporization from free surface) − (Rate out across adjacent screw flight) = 0. Thus

$$Q\frac{dC(z)}{dz} = -C(z)\left[2V_B\left(\frac{Dt_e}{\pi}\right)^{1/2} + \frac{V_B\delta}{2}\right] + C(z+\Delta)\left[\frac{V_B\delta}{2}(1-\gamma)\right] \quad (2)$$

In the above expression, γ is the fraction of the original solvent removed from the film that is dragged over the flight. If the penetration theory is valid, $\gamma = \frac{4}{\delta}\left(\frac{Dt_f}{\pi}\right)^{1/2}$. In general, γ may be calculated by using existing solutions for diffusion or heat conduction in finite slabs.

The quantity Δ in the above expression is the distance downstream at which the polymer that enters the control volume from over the downstream flight originates. This parameter is given by

$$\Delta = (\sqrt{\pi^2 d^2 + t^2}) + (t_f Q/Wfh)$$

A LIMITING CASE

If the land clearance δ is small, and if the exposure time t_f is large, the fraction γ will approach unity. Equation (2) then reduces to

$$\frac{dC(z)}{dz} = -\beta_1\, C(z) \quad (3)$$

where

$$\beta_1 = \left[2V_B\left(\frac{Dt_e}{\pi}\right)^{1/2} + \frac{V_B\delta}{2}\right] \Big/ Q \quad (4)$$

Equation (3) is subject to the boundary condition

$$C(z) = C_0, \quad z = 0 \quad (5)$$

where C_0 is the concentration of volatile material in the feed to the extruder so that

$$C(z) = C_0 e^{-\beta_1 z} \quad (6)$$

The diffusivity of volatile material in the polymer is then given by

$$D = \frac{\pi V_B}{h}\left[\frac{\left(-\ln\frac{C_f}{C_0}\right)Q}{2V_B L} - \frac{\delta}{4}\right]^2 \quad (7)$$

In the above expression, L is the length of screw channel in the extraction section. A value of L can be computed from the data of reference 3 by using the relationship L = (filled volume in extraction section)/(Wfh).

A GENERAL SOLUTION

Equation (2) may be written

$$\frac{dC(z)}{dz} = -\beta_1 C(z) + \beta_2 C(z+\Delta) \quad (8)$$

where β_1 is defined by Equation (4), and β_2 is

$$\beta_2 = \frac{V_B\delta(1-\gamma)}{2Q} \quad (9)$$

Equation (8) is also subject to the boundary condition given by Equation (5).

Equation (8) is a differential-difference equation of the advanced type, the exact solution of which is extremely difficult (*1*). The expedient of a series solution is therefore adopted. Expanding $C(z + \Delta)$ in a Taylor's series about z, we get

$$C(z+\Delta) = C(z) + \frac{dC(z)}{dz}\Delta + \frac{d^2C(z)}{dz^2}\frac{\Delta^2}{2} + H.O.T. \quad (10)$$

By neglecting third-order and higher terms (H.O.T.), Equation (8) becomes

$$\frac{d^2C(z)}{dz^2} - \left[\frac{2(1-\beta_2\Delta)}{\beta_2\Delta^2}\right]\cdot\frac{dC(z)}{dz} + \left[\frac{2(\beta_2-\beta_1)}{\beta_2\Delta^2}\right]\cdot C(z) = 0 \quad (11)$$

The above equation has the form of the well-known dispersion model for a first-order chemical reaction in a tubular reactor. An equation similar to Equation (11) has also been applied to volatile removal in extruders by Latinen (*5*). The advantage of the present treatment is that an independent estimate of the Peclet number is not required, as it is in Latinen's approach. However, the present model implies that the major source of backmixing is leakage over the screw flights.

The term $2L(1 - \beta_2\Delta)/\beta_2\Delta^2$ may be interpreted as an effective axial Peclet number. A consequence of Equation (11) is that the effective axial Peclet number will be a function of the efficiency of the devolatilization process. If all of the solvent is removed from the polymer that is dragged over the screw flights, that is, if $\gamma = 1.0$, the effective axial Peclet number is infinite. If no solvent at all is removed ($\gamma = 0$), the Peclet number has a minimum value. This minimum value was calculated for the runs of reference 3, assuming a land clearance δ of 10 mils, to lie in the region of 5 to 50. This constitutes reasonable agreement with Latinen's (*5*) value of about 5, which was measured in a nondevolatilizing extruder using tracer-injection techniques.

If the approximate boundary condition

$$C(z) \text{ finite as } z \to \infty$$

is applied along with Equation (5), the solution to Equation (11) is

$$C(z) = C_0 e^{\lambda_1 z}$$

$$\lambda_1 = \frac{(1-\beta_2\Delta)}{\beta_2\Delta^2}\left[1 - \left(1 - \frac{2(\beta_2-\beta_1)\beta_2\Delta^2}{(1-\beta_2\Delta)^2}\right)^{1/2}\right] \quad (12)$$

This approximate solution may be improved by noting that the integral of Equation (8) is

$$C(z) = C_0 + (\beta_2 - \beta_1)\int_0^z C(z)dz + \beta_2\int_z^{z+\Delta} C(z)dz - \beta_2\int_0^{\Delta} C(z)dz \quad (13)$$

Iterative application of Equation (13), together with some induction, yields

$$C_{n+1}(z) = E_{n+1}e^{\lambda_1 z} + \sum_{k=0}^{n-1} A_{k,n+1}z^k; \quad n \geq 1 \quad (14)$$

where the coefficients $A_{k,n+1}$ and E_{n+1} are defined by the recursion relations

$$A_{0,n+1} = C_0 - \frac{E_n}{\lambda_1}(\beta_2 e^{\lambda_1 \Delta} - \beta_1), \quad k = 0 \qquad (14a)$$

$$A_{k,n+1} = -\frac{\beta_1 A_{k-1,n}}{k} + \beta_2 \sum_{i=k}^{n-1} \frac{A_{i-1,n}}{i}\left(\frac{i!\,\Delta^{i-k}}{(i-k)!\,k!}\right), \quad 1 \leqq k \leqq n-1 \qquad (14b)$$

$$E_{n+1} = \frac{E_n}{\lambda_1}(\beta_2 e^{\lambda_1 \Delta} - \beta_1) \qquad (14c)$$

$$E_1 = C_0 \qquad (14d)$$

Equation (14) is inconvenient to use for calculating the diffusivity from experimental data, but it might be valuable for estimating the performance of an extruder from a known or assumed value of the diffusivity. The convergence properties of Equations (13) and (14) have not been investigated; convergence problems could limit the utility of these equations.

RESULTS AND DISCUSSION

The Relative Importance of Devolatilization Mechanisms

The preceding model permits a comparison of the importance of the two devolatilization mechanisms: vaporization from the free surface and vaporization from the land film. At any point in the extruder, and over the extruder as a whole, the percentage of the total vaporization that occurs in the land film is

$$\frac{1}{1 + \dfrac{4}{\delta\gamma}\left(\dfrac{Dh}{\pi V_B}\right)^{1/2}}$$

When the land film is thick enough, or the diffusivity is low enough, γ is accurately given by the penetration theory approximation quoted earlier, and the above expression reduces to

$$\frac{1}{1 + \left(\dfrac{1}{W(1-f)}\right)^{1/2}}$$

Calculations of the fraction of total vaporization that takes place in the land film were performed for a typical extruder geometry and operating conditions, similar to those given in reference *3*. The assumed parameters were: $h = 0.500$ in., $N = 90$ rev./min., $d = 4.50$ in., $W = 3.82$ in., and $f = 0.25$. Two values of δ, 0.05 and 0.010 in., were considered. Values of γ were calculated from the exact solution to the equation for unsteady state diffusion in a finite slab (*4*).

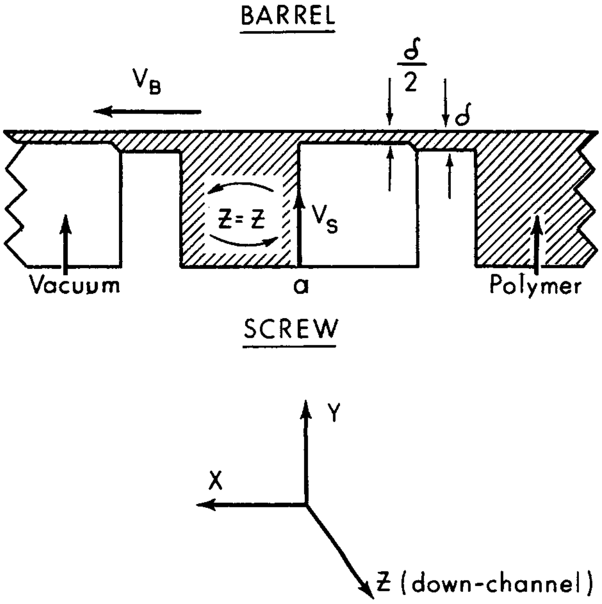

Fig. 1. Cross section of partially filled screw channel.

The results of the calculations are shown in Figure 2. Since the proper value of the diffusivity is under debate, the fractional vaporization from the land film is plotted as a function of the diffusivity. Figure 2 shows that unless the diffusivity is extremely high, vaporization from the land film plays a major role in volatile removal. For a diffusivity in the range of 10^{-3} to 10^{-4} in.^{2}/min., land film vaporization accounts for 60 to 70% of the total volatile removal.

TABLE 1. CALCULATED DIFFUSIVITIES
Diffusivity (in.^{2}/min.)

Run No.	Original value (*3*)	$\delta = 0$	$\delta = 5$ mils	$\delta = 10$ mils
1	1.76	0.0485	0.0330	0.0204
2	1.54	0.0283	0.0129	0.00345
3	2.28	0.0410	0.0183	0.00467
4	0.776	0.0123	0.00159	Negative
5	1.83	0.0387	0.0197	0.00709
6	1.74	0.0958	0.0787	0.0632
7	1.70	0.0661	0.0467	0.0307
8	1.18	0.0335	0.0176	0.00679
9	2.52	0.230	0.190	0.154
10	2.03	0.161	0.116	0.0776
11	2.22	0.183	0.142	0.107
12	2.90	0.321	0.272	0.227

Correlation of Experimental Data

Values of the diffusivity of the volatile material in the molten polymer were calculated, by using Equation (7), for each of the twelve runs of reference 3. A set of calculations was made for each of three different values of the land clearance δ. Results are shown in Table 1.

The calculations for $\delta = 0$ correspond to a situation where all volatile material is removed at the free surface. In this case, the effective diffusivities for the first eight runs are roughly a factor of 50 lower than the original values, but the values for the last four runs are lower by only about a factor of 10. Although these diffusivities are more reasonable than the original values (*3*), they still fall short of the region of about 10^{-3} to 10^{-4} in.^{2}/min. that might be expected from extrapolation of literature data (*5, 7*).

The second set of calculations was for a land clearance of 5 mils, which corresponds to a film thickness of 2.5 mils. Even if the diffusivity is very low, this thin a film will be almost completely stripped of volatile material. The use of Equation (7) is completely justified in this case. Table 1 shows that the reduction in the calculated diffusivity caused by including the effect of a 5 mil land clearance is generally small, except for run No. 4. For this experiment, the calculated diffusivity is only about a factor of 2 higher than the diffusivity reported (*5*) for styrene monomer in polystyrene at 500°C.

A land clearance of 10 mils was assumed in the last set of calculations. This value corresponds to the situation that might exist in an extruder that had been in use for some period of time. The film thickness for this case is 5 mils. At this thickness, the fractional devolatilization of the polymer film is quite dependent on the value of the diffusivity. If the diffusivity is as high as 10^{-2} in.^{2}/min., the fractional devolatilization is close to unity. However, for lower values, γ may be substantially less than unity. This case probably represents a liberal estimate of the amount of devolatilization that takes place in the land film.

Table 1 shows that the diffusivities for several additional runs have been brought down towards the proper order of magnitude by the use of a value of $\delta = 10$ mils. However, other runs, notably the last four, still have diffusivities that are several orders of magnitude too high. Further, the use of $\delta = 10$ mils overestimates the amount of devolatilization that occurred during run No. 4.

Some of the results given in Table 1 suggest that the proposed model can fit the experimental data of Coughlin and Canevari, consistent with a reasonable magnitude of the diffusion coefficient. However, other results are disappointing. Although all of the calculated diffusivities are an order of magnitude or more lower than the original values, the scatter of the present diffusivities is more pronounced than that of the original values.

There are a number of possible reasons that the experimental data offer only partial support for the proposed model. In the first place, a constant value of δ was assumed in each of the above sets of calculations. In reality, the land clearance probably varied substantially from screw to screw, and perhaps along the length of a given screw. Variation of δ could have contributed substantially to the observed scatter. Secondly, the value of L that was used in all of the calculations corresponded to exactly five screw flights; this number was calculated directly from the original data and probably corresponds to the design length of the extraction section. In practice, devolatilization is not necessarily confined to the extraction section. If the metering or pressure developing section is not filled with polymer over its whole length, vacuum can penetrate downstream of the extraction section, thereby extending the effective devolatilization length of the extruder. The exit solute concentration C_f will then be lower than if volatile removal had been confined to the extraction section. A calculation of the diffusivity based on actual data for C_f and a theoretical value of L will therefore lead to a high value of the diffusivity. If the effective length of the extraction section varies from run to run, scatter of the calculated diffusivities will result. Finally, another source of inconsistency may be the approximate treatment of polymer flow in the cross section of the extruder. If the free surface velocity is higher than assumed, and if it is not linearly related to the cross-channel component of barrel velocity, the calculated diffusivities will be high, and will scatter. A more rigorous analysis of the fluid dynamics of cross-channel flow might improve the theory.

CONCLUSIONS

A model for the devolatilization of polymers in single screw extruders has been presented which accounts for the renewal of exposed surface by the circulation of polymer melt in the cross section of the channel, and for the creation of devolatilization surface by flow over the flights of the screw. The latter can be a very important source of devolatilization, accounting for 50% or more of the total vaporization.

The data of reference 3 provide only partial support for the proposed model. Additional carefully controlled, experimental measurements of the rate of volatile removal in single screw extruders are necessary in order to confirm or deny the validity of the theory. These measurements should be accompanied by an independent experimental study of the diffusion of vapors in polymers at high temperatures in order to avoid the need to speculate concerning the appropriate value of the diffusion coefficient.

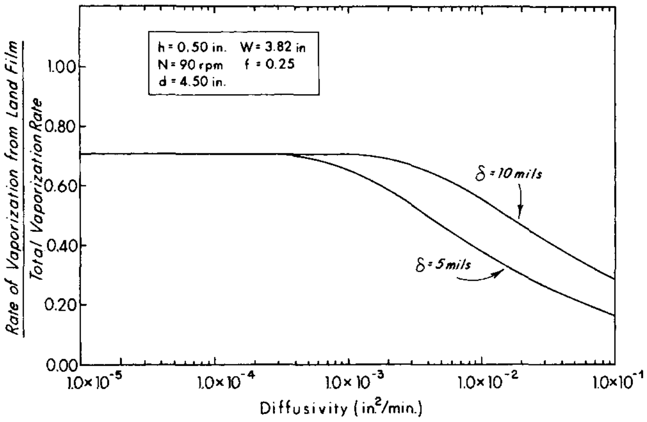

Fig. 2. The relative importance of vaporization from the land film.

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NOTATION

A = area of free polymer surface, in.^{2}
$A_{k,n+1}$ = coefficient in Equation (14), defined by Equations (14*a*) and (14*b*)
C = concentration of volatile material in the bulk of the polymer at any time, moles/in.^{3}
C_0 = initial concentration in the feed to the extruder, moles/in.^{3}
C_f = final concentration, moles/in.^{3}
D = diffusivity of volatile material in polymer, in.^{2}/min.
d = extruder diameter, in.
E = coefficient in Equation (14), defined by Equations (14*c*) and (14*d*)
f = fraction of channel filled
h = screw channel depth, in.
i = dummy variable [see Equation (14*b*)]
k = dummy variable [see Equations (14) and (14*b*)]
L = length of screw channel in extraction section, in.
N = screw rotational speed, rev./min.
n = iteration number [see Equation (14)]
Q = volumetric polymer flow rate, in.^{3}/min.
q_e = amount of solvent removed from unit surface of polymer in time t_e, moles/in.^{2}
t = time, min.
t_e = time for which polymer is exposed to vacuum at free surface, min.
t_f = time for which polymer in the land film is exposed to vacuum, min.
V_B = x component of polymer velocity at barrel surface, in./min.
V_s = y component of polymer velocity at free polymer surface, in./min.
V_y = y component of polymer velocity, in./min.
W = channel width perpendicular to flight faces, in.
x = distance measured perpendicular to free polymer surface, in.
y = distance measured perpendicular to barrel surface, in.
z = distance measured down the unwrapped screw channel, in.

Greek Letters

ϕ = helix angle
β_1 = parameter defined by Equation (4)
β_2 = parameter defined by Equation (9)
Δ = $\sqrt{\pi^2 d^2 + t^2} + (t_f Q/Wfh)$
δ = land clearance, in.
γ = fractional volatile removal from land film
λ_1 = parameter defined by Equation (12)

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Effect of Transport Processes on Conversion in a Fixed Bed Reactor

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For a first-order reaction in an isothermal, fixed bed reactor, it is relatively simple to show the combined effects of axial dispersion, fluid-to-particle diffusion, intraparticle diffusion, and surface reaction on the conversion. Apparently this has not been done. Yet, for the purpose of evaluating the effect of transport resistances, many important catalytic reactions can be described with pseudo first-order kinetics. Therefore, relations which directly display these effects on conversion could be helpful both for interpretation of laboratory kinetic studies and for industrial design. Figure 1 has been prepared for this purpose. It is based upon Equations (11) to (14) which are developed in the following paragraphs.

Recently (*8*), equations have been derived for the zeroth, first, and second moments of the reactant concentration in the effluent from a fixed bed reactor in response to a pulse introduced into the feed. These equations include the effects of all transport resistances and are restricted to isothermal operation and to first-order surface processes. The equation for the zeroth moment can be related to the conversion x at steady state with the result

$$1 - x = \frac{C}{C_0} = \exp\left[-\frac{uz}{2E_z}(\gamma^{1/2} - 1)\right] \qquad (1)$$

where

$$\gamma = 1 + \frac{4E_z k_f}{u^2}\left(\frac{3(1-\alpha)}{\alpha}\right)$$
$$\left\{1 - \frac{k_f R_p/D_e}{R_p\sqrt{k_r\beta/D_e}\,\coth\,(R_p\sqrt{k_r\beta/D_e}) - 1 + k_f R_p/D_e}\right\} \qquad (2)$$

This result can also be obtained by solving the steady state version of the problem. The solution, Equations (1) and (2), can be written in the following form, which is more convenient for displaying the effects of the transport processes:

$$1 - x = e^{-\Lambda_3\omega} \qquad (3)$$

$$\Lambda_3 = \frac{N_{Pe}}{2}[\sqrt{1 + 4\,\Lambda_2/N_{Pe}} - 1] \qquad (4)$$

$$\Lambda_2 = \frac{1}{1/\Lambda_1 + 1/S} \qquad (5)$$

$$\Lambda_1 = \frac{3}{F}[\sqrt{\Lambda_0 F}\,\coth\,(\sqrt{\Lambda_0 F}) - 1] \qquad (6)$$

Here Λ_2 is a dimensionless global rate of reaction which includes the effects of external mass transfer (S), intraparticle diffusion (F), and surface rate (Λ_0).

When axial diffusion is negligible, N_{Pe} is large with respect to Λ_2 so that $\Lambda_3 \approx \Lambda_2$. If intraparticle diffusion resistance is negligible, F is so small that $\Lambda_1 \approx \Lambda_0$ from Equation (6). When external mass transfer resistance is negligible, S is large compared with Λ_1 so that $\Lambda_2 \approx \Lambda_1$. If all three transport resistances are negligible, $\Lambda_3 \approx \Lambda_0$, and Equation (3) is the usual expression for the conversion in terms solely of the kinetics of the reaction. In general, Λ_3 may be regarded as a pseudo global rate, which includes the effect of axial dispersion as well as the other transport processes.

Well known results for particular cases follow directly from Equations (3) to (6). For example, the effectiveness factor η of Thiele (*9*) is given by the ratio Λ_1/Λ_0. External diffusion has been included as an overall effectiveness factor η_{ov} by Carberry (*1*). This is given by the ratio Λ_2/Λ_0, modified to apply to flat plate geometry. Ruthven (*7*) included external diffusion by using a mass transfer factor η'. This is obtained from Equations (5) and (6) as the ratio Λ_2/Λ_1.

Figure 1 is a graphical representation of Equations (3) to (6), where each section displays the effect of a single transport resistance. Section A shows the relation between Λ_1 and Λ_0, or the importance of intraparticle diffusion; section B relates Λ_1 and Λ_2, indicating the importance of external diffusion; section C compares Λ_2 and Λ_3 and so gives the effect of axial dispersion. In using Figure 1 to evaluate the significance of the transport resistances, the kinetic constant k_r or k_B would be known so that Λ_0 can be calculated. Then the effect of each transport process could be estimated from estimates of F, S, and N_{Pe}. Section D of the figure shows the resultant effect of all the transport processes on the conversion in the effluent from the reactor. Figure 1 should also be useful for a rapid estimate of the kinetic constant from the observed conversion. In this case, x would be known, and the figure would be used in the reverse direction, proceeding from section D to C to B to A in order to eliminate the transport effects and arrive at Λ_0.

The oxidation of *o*-xylene to phthalic anhydride is used