Stability of Multislit Devolatilization of Polymers

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Slit devolatilization of polymers has been considered in a recent work by Maffettone et al. (1991), who have presented a successful model for single slit devolatilization. In this article, the stability of operation of a realistic multislit process is considered. It is shown that the flow rate per slit which can be stably operated may be significantly less than the optimal one for single slit operation. Stability improves as the concentration of volatiles in the feed solution decreases. The non-Newtonian character of the feed solution at high shear rates is discussed in qualitative terms.

Introduction

Maffettone et al. (1991) have published a model for single slit devolatilization of polymers. The model contains only one adjustable parameter, and it is surprisingly successful in predicting experimentally measured profiles of concentration of volatile, temperature, and pressure along the slit, in spite of the fact that the viscosity of the liquid may change by several orders of magnitude along the slit.

The model was tested only for conditions similar to the experimental ones, which were in fact in the region of flow rates low enough that devolatilization is still efficient, but high enough that the efficiency criterion is just barely met. (Since the slit is modeled as equivalent to two infinite parallel plates, flow rates are always intended per unit width.) The actual flow rate which can be achieved in a single slit under acceptable devolatilization conditions is quite low for an actual industrial process, and the latter is in fact realizable only by means of a multislit configuration. Typically, an industrial unit consists of several thousand slits in parallel.

While in the case of a single slit fed with a fixed volumetric flow rate of the polymer solution the flow conditions are invariably stable, this is not necessarily the case in a multislit configuration. In the latter case, the total flow rate Q_T is imposed on the system, and, if there are N slits, stable operation corresponds to the situation where the flow rate in every slit, Q, is (at least approximately) Q_T/N. Since vacuum is imposed at the slits exit, and pressure in the feed chamber is very nearly constant, the pressure drop J (which is very nearly equal to the feed chamber pressure) is the same in all slits; this, however, as will be seen below, does not guarantee that the flow rate is also the same in all slits.

This point has been discussed by Lynn and Oldershaw (1984) in their analysis of a multislit process where only heat transfer occurs (no devolatilization). It is useful to present here the essence of the Lynn and Oldershaw analysis, which of course will need to be generalized to include the effect of devolatilization. Let T_0 and T_W be the feed and slit wall temperatures, respectively. If heat transfer is the only phenomenon taking place, the polymer viscosity is a unique and monotonously decreasing function of the local temperature, $\mu = \mu(T)$, $d\mu/dT < 0$. At extremely small flow rates, the slit is grossly overdesigned for heat transfer, and hence $T \approx T_W$ over practically the whole slit length. Hence the viscosity is also constant, and the pressure drop J is proportional to the product $\mu(T_W)Q$. Conversely, at very high flow rates the slit is grossly underdesigned for heat transfer, and hence $T \approx T_0$, and J is proportional to $\mu(T_0)Q$: both asymptotes are straight lines through the origin. If the polymer is being heated ($T_W > T_0$), the high flow rate line lies above the low flow rate one, and hence the whole J vs. Q curve is monotonously increasing. However, in cooling the converse is true, and the J vs. Q curve may exhibit both a maximum and a minimum, as shown in the sketch in Figure 1.

When the situation in Figure 1 occurs, operation of a multislit configuration may be unstable, because there is a range of pressure drop values (between the maximum and the minimum), where three different flow rates are possible. Let $J = l(Q)$ represent the curve in Figure 1, with $l'(Q)$ being its ordinary derivative. Since the pressure drop is the same for all slits, it is imposed on any one slit by the combined effects of

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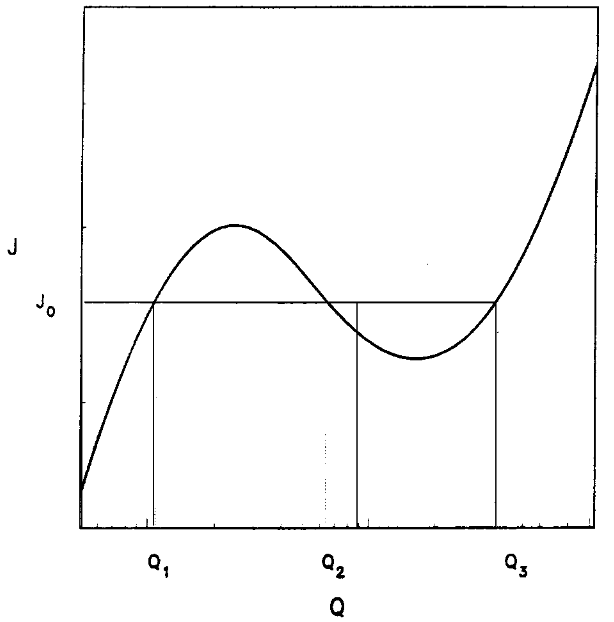

Figure 1. Qualitative sketch of the curve J vs. Q in the logarithmic plane.

all the other ones; let J_0 be the imposed value, such that the horizontal line $J=J_0$ crosses the curve three times at values Q_I, $I=1, 2, 3$. Suppose that the actual flow rate is displaced from one of the steady state values Q_I by an amount δQ, $Q=Q_I+\delta Q$. The pressure drop corresponding, at steady state, to Q is:

$$J=J_0+l'(Q_I)\delta Q+O(\delta Q^2) \tag{1}$$

where, in a linear stability analysis, only terms of order δQ are retained. Since the actual pressure drop J_0 is different from the one arising from friction at the walls, the difference causes acceleration of the polymeric phase in the slit, and hence one may write:

$$J_0-J=-l'(Q_I)\delta Q=K\,dQ/dt=K\,d\delta Q/dt \tag{2}$$

where K is a positive constant. It follows that:

$$\mathrm{sgn}[(1/\delta Q)d\delta Q/dt]=-\mathrm{sgn}[l'(Q_I)] \tag{3}$$

The intersection is a stable one if $\mathrm{sgn}(d\delta Q/dt)=-\mathrm{sgn}(\delta Q)$, and hence if $l'(Q_I)>0$. It follows that the middle one of the intersections is infinitesimally unstable and will therefore never be observed in actual operation. Conversely, both the left and right intersections are locally stable, and hence a multislit configuration may well operate with some slits in the low flow rate mode and some in the high flow rate one. This is a locally stable, but unacceptable mode of operation, since devolatilization in the slits operating in the high flow rate mode would be very inefficient.

Now consider the J vs. Q curve for the case where devolatilization may take place (in this case, T_0 is certainly less than T_W, since the process is of interest for the very reason that the polymer is exposed to high temperatures only for short periods of time). The liquid viscosity, however, now depends on both temperature and polymer mass fraction c, $\mu=\mu(T, c)$. The dependence on c is a very strong one, so that, due to devolatilization the viscosity may change by several orders of magnitude over the slit length, and in fact it will almost invariably increase along the flow direction, in spite of the fact that temperature is also increasing, because the effect of an increasing c more than overcomes that of the temperature raise. One is therefore always in a condition analogous to the cooling one of the Lynn and Oldershaw analysis, which may well yield an instability.

Asymptotic behaviors of the J vs. Q curve for very large and very small flow rates can again be established, although in this case they are indeed asymptotes holding only for *extremely* low or high flow rates. First consider the case of very low flow rates. Again one may take $T=T_W$ over practically the whole slit length. Mass transfer is also very efficient, and hence the volatile concentration is everywhere equal to the equilibrium value corresponding to the local pressure. Furthermore, at vanishingly small flow rates the pressure drop is also vanishingly small and hence pressure is practically equal to the exit pressure everywhere. It follows that the viscosity of the liquid is, almost everywhere, $\mu(T_W, c_F)$, where c_F is the (very high) polymer concentration at the slit exit. Thus J is proportional to $\mu(T_W, c_F)Q$: one again has a low flow rate straight line asymptote, but the line has a very large slope. (As will be discussed later, although this asymptote emerges from the model equations, it has no physical significance and is used here only as an internal check of the solution procedure).

Now consider the case of extremely large flow rates (again, there are some subtleties which will be discussed later). In this limit, practically no heat transfer takes place, and hence the temperature is that of the feed solution, T_0, over the whole slit length. By the same token, also mass transfer is practically absent, and hence the polymer mass fraction is approximately equal to the feed value c_0 everywhere. It follows that the viscosity is again constant and equal to $\mu(T_0, c_0)$. Whatever the temperature difference T_W-T_0 might be, the dominating factor is the volatile concentration, which in this limit is quite large; it follows that the liquid viscosity is very low. The high flow rate asymptote is again linear, but the slope is a few orders of magnitude less than that corresponding to very low flow rates. One may therefore have an instability of the same type as the one discussed by Lynn and Oldershaw for the multislit cooling process, in spite of the fact that the polymer is in fact being heated in the slits.

The consequences of such an instability are rather drastic ones. First consider the case of a single slit. Maffettone et al. (1991) have shown that the optimum flow rate is in fact close to the one corresponding to the maximum pressure drop: the leakage rate of volatile is in fact still acceptable up to approximately that point. However, that flow rate is guaranteed to be in the region of instability, and in fact the largest possible stable flow rate in a multislit configuration may well be significantly less than the optimum one for single slit operation.

In this article, we analyze the multislit instability for a devolatilization process. In doing so we use as a basis the model developed by Maffettone et al. (1991). However, since we need to establish the form of the J vs. Q curve over the whole range of possible Q values, rather than only in the range of significant single slit experiments, the model needs a substantial modification. Maffettone et al., when analyzing the heat-transfer phenomenon, observed that, in the range of experiments, the Graetz number was invariably small (most of the slit length is used for devolatilization, not for heating), and hence they used the asymptotic value of the Nusselt number corresponding to low Graetz numbers. This is not an acceptable approximation at large flow rates, and hence one needs to solve the unsteady heat conduction equation in the liquid phase. The resulting model is of course a two-dimensional one, in contrast with the essentially one-dimensional formulation of Maffettone et al.

The system we consider is the same one as analyzed by Maffettone et al. (1991): ethylbenzene (volatile) in polystyrene (MW 300,000, MW/MN = 2). The physical properties of these solutions are reported by Maffettone et al.; we have also used their correlations for the polymer phase viscosity and the volatile vapor pressure.

A final observation of a general nature is in order. Most of the analyses of devolatilization processes reported in the literature entirely neglect the heat-transfer phenomenon, which however plays a crucial role in the present analysis. Now suppose that no heat is supplied to the polymeric phase from the walls of the apparatus; in this case the polymeric phase would cool down adiabatically due to the devolatilization effect. If δc is the change in volatile mass fraction from the inlet to the outlet, Γ the latent heat, and c_P the polymer specific heat, the adiabatic cooling would be $\Gamma\delta c/c_P$. For the ethylbenzene-polystyrene system, which is in no way atypical from this viewpoint, Γ/c_P is of the order of 200 C. It follows that, except in tail operations (where devolatilization is carried out from a polymeric phase which has already been reduced to a very low value of volatile concentration in the preceding steps, so that δc is a very small number), the adiabatic cooling would be too large, resulting in a rapid quenching of the devolatilization process. It follows that heat does indeed need to be supplied from the walls of the apparatus, at a sufficiently high rate to compensate for the latent heat of devolatilization.

Model Equations

Many of the model equations are the same as given by Maffettone et al. (1991), and are discussed only concisely below. In particular, all the geometrical approximations used by Maffettone et al. are retained here, and they are not discussed again. Let P and G be the mass flow rates of the polymeric and the gas phase, respectively; c the mass fraction of polymer in the liquid phase; x the distance from one of the bounding walls of the slit, and y the axial distance from the slit entrance section. P, G and c are local (y-dependent) values. The overall and the polymer mass balances yield immediately:

$$P+G=Q \tag{4}$$

$$Pc=Qc_0 \tag{5}$$

Maffettone et al. (1991) have discussed in detail several approximations, which are of a general nature. The slit thickness H is significantly less than the slit transverse width, and therefore the slit can be approximated as two parallel plates; the central gas layer thickness, although variable along the slit, is everywhere negligibly small as compared to H, and it can therefore be neglected whenever appropriate. These approximations are made here as well, and the polymer phase momentum balance yields the local pressure gradient:

$$-dp/dy=12\mu P/H^3\rho=12\mu Qc_0/H^3c\rho \tag{6}$$

where ρ is the polymer density (here regarded as constant).

The axial pressure gradient can be eliminated between Eq. 6 and the momentum balance in the gas phase to yield an expression for the local value of the gas layer thickness h (this is not really needed for the problem at hand, but is reported for the sake of completeness; ϵ is the ratio of kinematic viscosities of gas and polymer):

$$h^3/H^3=\epsilon G/P \tag{7}$$

The polymer phase velocity distribution is:

$$v(x,y)=(6P/\rho H^3)(Hx-x^2) \tag{8}$$

This was given, but in actual fact not used, by Maffettone et al. (1991); here we make crucial use of it in the heat balance equation to be discussed below.

Mass transfer is modeled in the same way as done by Maffettone et al. (1991), with the only adjustable parameter of the model, A, as appearing below. Let $f(T, c)$ be the vapor pressure of the volatile at temperature T and polymer mass fraction c, and let T^* be the *average* temperature over a cross section. The mass-transfer equation is written as:

$$-dP/dy=-Qc_0d(1/c)/dy=A[f(T^*,c)-p] \tag{9}$$

This should be discussed in some detail. In the heat balance equation to be discussed below, temperature is regarded as depending on both x and y—as discussed previously, our model is a two-dimensional one. However, given the intrinsic crudeness of the assumption underlying the mass-transfer equation, we only take the cross-sectional average of T in its expression. Analogously, we also regard the polymer mass fraction c as averaged over the cross-section, so that physical properties like the polymer phase viscosity and the volatile vapor pressure are regarded as uniform over the cross-section. Indeed, Eq. 8 gives the correct transverse distribution of velocities only if the viscosity is regarded as uniform in the cross-section.

We now come to the two-dimensional heat-transfer equation. This must be written with great care. It obviously involves three terms (in addition to the frictional heating term to be discussed later): one representing convection in the axial direction (as usual in Graetz-like problems, heat conduction in the flow direction is neglected), one representing conduction in the transverse direction, and one representing the effect of devolatilization. The conduction term is obviously $k\partial^2T/\partial x^2$. The other two terms present some subtlety.

First consider the effect of the local rate of devolatilization. Let T° be the (arbitrarily chosen) temperature at which the liquid phase enthalpy is assigned the value zero. The specific heats per unit mass of the polymer and gas phases, c_P and c_G, are assumed to be constant: this assumption simplifies, but is in no way crucial to the argument below. Let Γ be the enthalpy of vaporization temperature T°. The enthalpies of the polymer and gas phases at temperatures T and T_G, respectively, are $c_P(T-T^\circ)$ and $\Gamma+c_G(T_G-T^\circ)$. Notice that this implies that the equilibrium enthalpy of vaporization at temperature T is $\Gamma+(c_G-c_P)(T-T^\circ)$. Notice also that the choice of T° is arbitrary, and for the sake of simplicity we choose it to be T_0, the temperature of the feed. Of course, since the enthalpy of vaporization of the system considered depends on temperature (Watson, 1943), (slightly) different values of Γ need to be used for different feed temperatures. Let $m(x, y)$ be the mass of volatile which devolatilizes per unit volume and time. Then, the local rate of heat removal in the polymer phase due to devolatilization is $m(x,y)[\Gamma+c_G(T_G-T_0)-c_P(T-T_0)]$. The quantity $m(x, y)$ needs still to be determined.

The average value of $m(x, y)$ over the whole cross-section, $m^*(y)$, is of course $-(\partial P/\partial y)/H$. What the actual distribution of m values over the cross section might be is of course not known, and one could choose the crude approximation that it is uniform, $m=m^*$. However, this creates a slightly bothering conceptual problem which is discussed below. (It should also be noted that, if one takes m to be m^*, one runs into subtle difficulties when trying to obtain by integration the correct heat balance averaged over the cross section, say Eq. 17 below).

The local flow rate per unit cross-sectional area is of course $\rho v(x, y)$, and hence the local change of flow rate along the flow direction is $\rho\partial v/\partial y$. From this viewpoint, one would calculate $m=-\rho\partial v/\partial y$. It follows that the assumption of a uniform value of m in the cross-section would imply the insurgence of a secondary flow (a small but nonzero value of the x component of velocity). Conversely, the assumption that there is no secondary flow implies that the m distribution along x is parabolic (proportional to the v distribution). This, as a distortion of the crude assumption of uniformity, is at least in the right direction, because devolatilization is likely to be more easy as one moves towards the gas phase. We have performed a few calculations with both expressions for m (neglecting entirely the secondary flow in the case $m=m^*$), and the difference is very slight. The results reported below are all based on the assumption of no secondary flow, say the devolatilization term is written as $-\rho(\partial v/\partial y)[\Gamma+c_G(T_G-T_0)-c_P(T-T_0)]$.

Since the effect of a local rate of change of polymer phase flow rate has already been accounted for in the devolatilization term, the convection term can be written in the usual form $\rho c_P v\partial T/\partial y$. Hence the heat balance differential equation takes the form:

$$\rho c_P v\,\partial T/\partial y=k\,\partial^2T/\partial x^2+[\Gamma+c_G(T_G-T_0)-c_p(T-T_0)]\rho\,\partial v/\partial y \qquad (10)$$

The cross-sectional average temperature T^* is defined as the mixing cup temperature of the polymer phase, say:

$$T^*(y)=(2\rho/P)\int_0^{H/2} v(x,y)T(x,y)dx \qquad (11)$$

Equations 6, 9, and 10 are a system of coupled differential equations for the one-dimensional dependent variables $c(y)$, $p(y)$ and for the two-dimensional temperature distribution $T(x, y)$ (the velocity distribution $v(x, y)$ is separately known, see Eq. 5). With L the slit length, the following trivial boundary conditions can be written:

$$c(0)=c_0 \qquad (12)$$

$$p(L)=p_0 \qquad (13)$$

$$T(x,0)=T_0 \qquad (14)$$

$$T(0,y)=T_W \qquad (15)$$

Before writing the last boundary condition, it is useful to note that, since Eq. 13 imposes a condition at the exit, while the other conditions are imposed at the entrance, the problem is a two-point boundary value one. This can be addressed either by the method of weighted residuals, or by a shooting technique involving a convergence loop. We have chosen the latter technique.

The last boundary condition is written at the polymer-gas interface, which, to within the same geometrical approximations which have already been used implicitly, can be regarded as being located at $x=H/2$ (rather than $x=(H-h)/2$). The heat flux towards the gas phase must balance the local rate of heating of the gas phase. Since the thickness of gas phase is extremely small, it is reasonable to assume that there are no transverse temperature gradients in it, and therefore the local average gas temperature is simply the interface temperature of the polymer phase, $T_G(y)=T(H/2, y)$. Hence:

$$x=H/2,\quad -2k\,\partial T/\partial x=c_G G\,\partial T/\partial y \qquad (16)$$

Let $q_W(y)=-k\partial T(0, y)/\partial x$ be the heat flux at the wall. With B.C. (Eq. 16), integration of Eq. 10 term by term between $x=0$ and $x=H/2$ yields, after algebraic rearrangement:

$$2q_W=c_P P\,dT^*/dy+c_G G\,dT_G/dy+[\Gamma+c_G(T_G-T_0)-c_P(T^*-T_0)]dG/dy \qquad (17)$$

This is quite obviously the correct local overall heat balance—the (equal) heat fluxes at the two walls are balanced by the rate of heating of the two phases, and by the enthalpy change due to devolatilization.

In the heat balance equation, the frictional heating contribution has been neglected. This approximation was also used by Maffettone et al. (1991), and it was justified by the fact that the frictional heating is at most 0.1% of the latent heat of devolatilization. In the range of parameter values considered by Maffettone et al., devolatilization was always significant, and hence the comparison is the correct one. Here however we wish to extend the calculation to large values of the flow rate, when devolatilization may well be only a minor phenomenon; hence neglect of the frictional heating term needs to be justified, at least at high flow rates, by comparison of its value with that of the heat conduction term. At large flow rates, however, the viscosity is low, and hence so is the frictional heating, and indeed the Brinkman number turns out to be at most 0.01, thus again justifying the neglect of the frictional heating term in the heat balance equation.

The following independent (z, u) and dependent (β, w, Θ) dimensionless variables are defined:

$$z=y/L \qquad (18)$$

$$u = x/H \tag{19}$$

$$\beta = p/p_0 \tag{20}$$

$$w = P/Q \tag{21}$$

$$\Theta = (T - T_0)/(T_W - T_0) \tag{22}$$

A dimensionless vapor pressure function $F(\,)$, and a dimensionless viscosity function $\sigma(\,)$, are defined as:

$$F(\Theta, c) = f(T, c)/p_0 \tag{23}$$

$$\sigma(\Theta, c) = \mu(T, c)/\mu(T_0, c_0) = \mu(T, c)/\mu_0 \tag{24}$$

Five dimensionless groups emerge from the equations: a dimensionless mass-transfer coefficient E, a dimensionless exit pressure U, a modified Graetz number Gz, a Stefan number St, and a specific heat ratio γ:

$$E = Ap_0L/Q \tag{25}$$

$$U = \rho p_0 H^3/L\mu_0 Q \tag{26}$$

$$Gz = Hc_PQ/kL \tag{27}$$

$$St = \Gamma/c_p(T_W - T_0) \tag{28}$$

$$\gamma = c_G/c_P \tag{29}$$

The dimensionless formulation of the problem is:

$$E[F(\Theta^*, c) - \beta] = c_0\, d(1/c)/dz \tag{30}$$

$$-U d\beta/dz = 12\sigma(\Theta^*, c)c_0/c \tag{31}$$

$$wc = c_0 \tag{32}$$

$$(u - u^2)\partial\Theta/\partial z = (1/6c_0Gz)c\,\partial^2\Theta/\partial u^2 + c[St + \gamma\Theta_G - \Theta](u - u^2)\, d(1/c)/dz \tag{33}$$

where Θ_G is of course $\Theta(1/2, z)$. The dimensionless cross-sectional average temperature Θ^* is given by:

$$\Theta^*(z) = 12\int_0^{1/2} (u - u^2)\Theta(u, z)du \tag{34}$$

The dimensionless boundary conditions are:

$$c(0) = c_o \tag{35}$$

$$\beta(1) = 1 \tag{36}$$

$$\Theta(u, 0) = 0 \tag{37}$$

$$\Theta(0, z) = 1 \tag{38}$$

$$u = 1/2, \quad -\partial\Theta/\partial u = (\gamma Gz/2)(1 - c_0/c)\partial\Theta/\partial z \tag{39}$$

Let r be the dimensionless heat flux in the u direction, say:

$$r = qL/c_PQ(T_W - T_0) \tag{40}$$

The dimensionless form of Fourier's law becomes:

$$Gzr = -\partial\Theta/\partial u \tag{41}$$

One may now integrate Eq. 33 over u from 0 to 1/2, and use Eq. 39 to obtain, after rearrangement:

$$2r_W = wd\Theta^*/dz + \gamma(1 - w)d\Theta_G/dz + [St + \gamma\Theta_G - \Theta^*]d(1 - w)/dz \tag{42}$$

which is the correct dimensionless heat balance over the whole cross section, r_W being the dimensionless heat flux at the wall.

The equations written above hold in the region where devolatilization does in fact occur, say the slit region near the exit where $f(T^*, c) > p$, or, equivalently, $F(\Theta^*, c) > \beta$. Near the entrance of the slit there is a region (which at high flow rates may extend almost to the very end of the slit) where no devolatilization occurs; this has been termed by Maffettone et al. as "the heating section." In the heating section $c = c_0$, $w = 1$, and the problem considered here reduces to the classical Graetz problem of heat transfer to a fluid in laminar flow in a slit. This has an analytical solution (Drew, 1931), which can be satisfactorily represented with simple power law expressions as given by Shah and London (1978) for the local Nusselt number and by Brown (1960) for the local transverse distribution of Θ. The latter have been used for the heating section (with the local pressure gradient calculated from the local viscosity), and the full numerical procedure has been started from the value of z at which $F(\Theta^*, c_0)$ becomes equal to β.

Asymptotic Behavior

We are now in a position to discuss more thoroughly the asymptotic behavior of the system considered. First consider the case of very large flow rates. As Q approaches ∞, both the inverse of the Graetz number appearing in Eq. 33 and the dimensionless mass-transfer coefficient E approach zero; it is therefore important to ascertain which one (if any) may be regarded as negligible first. In order to do so, we first analyze Eq. 30. The RHS is of the order of $\delta c/c_0$, where δc is the total change of c in the slit. It follows that devolatilization may be neglected ($\delta c \ll c_0$) if the LHS is much less than unity. Thus E may be regarded as being negligibly small if it is much less than the order of magnitude of $1/(F - \beta)$. Now β is unity at the slit exit, while F is of order of $F(0, c_0) = F_0$ which is, under realistic conditions, well in excess of unity. One concludes that the condition for regarding the flow rate as large enough that only minor devolatilization takes place is $EF_0 \ll 1$, which is much more stringent than $E \ll 1$.

Now we turn attention to Eq. 33. The LHS is of order $\delta\Theta$, the total change of dimensionless temperature along the slit length. Let z^* be the length of the heating section. At $z < z^*$, the second term on the RHS of Eq. 33 is zero, and hence $\delta\Theta$ in the heating section is negligibly small if $Gz \gg 1$. At $z > z^*$ the second term on the RHS is nonzero, and its order of magnitude is $St\delta c/c_0$. Thus heat transfer from the walls may be neglected if $1/Gz \ll 6StEF_0$. Hence, for sufficiently large values of St, there is a range of flow rate values where heat flux from the walls may be neglected but the devolatilization phenomenon is still of significance. This situation is analyzed below.

Equation 33 shows clearly that the high Graetz number limit is a *singular* one: the coefficient of the highest order derivative approaches zero (Nayfeh, 1973). In principle, this would require a boundary layer analysis. However, the "outer" solution is the only one that needs to be considered, since the boundary layer develops near the entrance to the slit where Boundary Condition 37 cannot be satisfied by it. In the outer solution, Θ is in fact only a function of z, and Eq. 33 reduces to:

$$d\Theta/dz = c[St + (\gamma - 1)\Theta]d(1/c)/dz \tag{43}$$

where use has been made of the fact that Θ^* and Θ_G are both equal to $\Theta(z)$. Equation 43 simply states the fact that, when heat transfer from the walls is negligible, the system undergoes adiabatic cooling to compensate for the rate of devolatilization.

Let the pressure at z^* be $\beta^* = \beta(z^*)$. In the heating section, $c = c_0$ and $\Theta = 0$; it follows that $\sigma = 1$, and that:

$$\beta^* = F(0, c_0) = F_0 \tag{44}$$

One may now integrate Eq. 31 first between $z = 0$ and $z = z^*$, and then between $z = z^*$ and $z = 1$ (the main section) to obtain the dimensionless total pressure drop:

$$\beta(0) - 1 = 12z^*/U + (12c_0/U)\int_{z^*}^{1} [\sigma(\Theta, c)/c]dz \tag{45}$$

The second term on the RHS of Eq. 45 equals $\beta^* - 1$, with β^* given by Eq. 44; this condition determines in principle the value of z^*. Now as long as EF_0 is not negligibly small, $\sigma(\Theta^*, c)/c > 1/c_0$, and it decreases towards $1/c_0$ as the flow rate increases. Since the integral has a fixed value, this implies that, in this region of moderately large flow rates, z^* decreases with increasing flow rates (contrary to what happens at low and at very high flow rates). It also implies that the first term on the RHS of Eq. 45 decreases with increasing flow rates, that is, that the final asymptote is reached from above. In fact, when EF_0 becomes negligibly small, $\sigma(\Theta^*, c)/c \approx 1/c_0$, and one obtains the result which was qualitatively presented in the introduction, which, in dimensionless form, is:

$$\beta(0) - 1 \approx 12/U \tag{46}$$

The converse case where the value of St is sufficiently small is significantly easier. The condition $EF_0 \ll 1$ is now met before heat transfer from the walls becomes negligible. After that, practically no devolatilization occurs, and the problem collapses to the heating case of the Lynn and Oldershaw (1984) analysis, where the final asymptote, which is still given by Eq. 46, is now reached from below. From the viewpoint of analysis, it is unfortunate that for the problem at hand the value of St is of order unity, so that one cannot foresee theoretically whether the final asymptote is in fact reached from above or from below. It is however of interest to observe that, from a practical viewpoint, the Stefan number is bound to be of order unity in the range of parameter values of pragmatic relevance (Astarita and Maffettone, 1992).

Now consider the other asymptote where the flow rate is very small. The discussion in the introduction was based on the implicit assumption that the inlet pressure may be as low as one wishes. This, however, is not in actual fact true: the dimensionless inlet pressure $\beta(0)$ must be larger than F_0, because otherwise there would be a driving force for devolatilization in the feed chamber, which might result in the formation of a foam at the inlet of the slits, and one could not assume any more that the polymer mass fraction at the slit inlet is equal to the feed value. We have however assumed in our model equations that such is indeed the case (that is, that for reasons left unexplored no devolatilization may occur in the feed chamber). This assumption is of course not realistic, but it is such that the low flow rate asymptote discussed in the introduction becomes a proper asymptote of the calculated solution. This offers the advantage that an inner check of the whole analysis is provided by the requirement that it should degenerate asymptotically to this (physically unrealistic) limit. The (physically realistic) condition that $\beta(0)$ should not be less than F_0 determines the lowest value of the flowrate for which our solution has physical meaning.

Results and Discussion

The set of differential equations has been numerically integrated on an IBM RISC 6000 machine using a finite difference approach. A Du Fort-Frankel scheme has been used to integrate the heat equation (Forsythe and Wasow, 1960; Shah and London, 1978). Although this scheme is explicit, it is unconditionally stable for linear equations: it treats a parabolic equation as a fictitious hyperbolic one in order to remove the source of instability. The ordinary differential equations have been integrated using a simple Euler method, because the computer capabilities allowed us to use very fine meshes with reasonable computation times. The results presented in the following have been obtained with an error of 10^{-3}. Details on the numerical procedure are given by Ianniruberto (1992) and Maffettone (1993).

Figure 2 presents the effect of the inlet mass fraction of polymer c_0 on the instability phenomenon. Notice that, other things being equal, the value of c_0 influences the position of the high flow rate asymptote (HFA), but not that of the low flow rate (LFA) one: the three curves coalesce at low flow rates. At a c_0 value of 0.5 the instability is quite marked; the largest stable flow rate per slit in the multislit configuration is 3.5×10^{-3} Kg/msec, while the optimal one for single slit operation is 1.3×10^{-2} Kg/msec. As c_0 increases, the minimum and maximum values of J become closer to each other, until at $c_0 = 0.7$ the instability phenomenon has totally disappeared.

Notice that the z^* vs. Q curve does not have a decreasing part (Figure 3), that is, that from the viewpoint of the asymptotic analysis discussed earlier the Stefan number is small (a typical value is 3). There is a hint of a tendency to develop a decreasing branch of the z^* curve at the highest initial concentration, however, indicating that the Stefan number is only marginally small. This is confirmed by the fact that the HFA is reached from below (Figure 2).

Figures 4 and 5 give the average temperature in the slit, and the exit mass fraction of volatile as a function of flow rate.

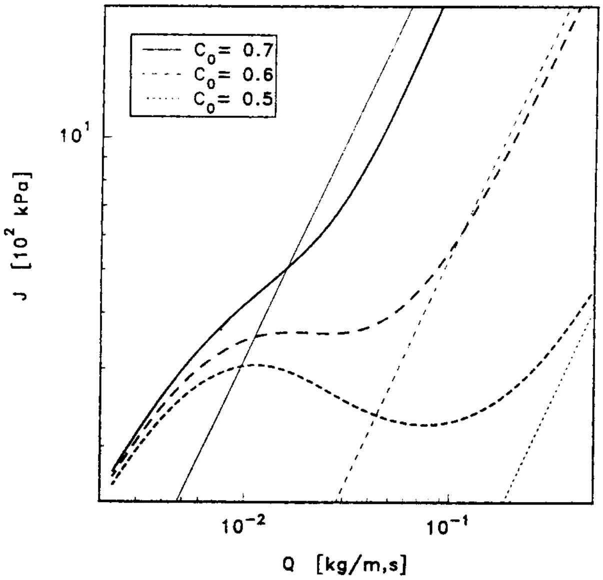

Figure 2. Pressure drop *J* vs. the flow rate *Q* for different values of the polymer concentration at the inlet.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $T_0 = 431$ K, $T_W = 533$ K).

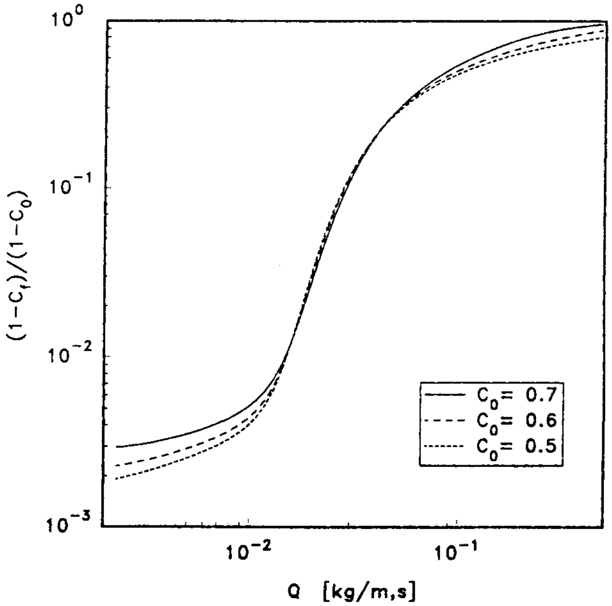

Figure 4. Volatile concentration at the slit exit against the flow rate for three different values of the polymer concentration at the inlet.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $T_0 = 431$ K, $T_W = 533$ K).

Devolatilization becomes negligible at flow rates of the order of 10^{-1} kg/m·s (Figure 4) while the average temperature approaches the wall temperature at flow rates of the order of 5×10^{-1} kg/m·s (Figure 5), so that indeed there is a range of Q values where the only phenomenon is the heating of the polymer phase.

This is also confirmed by the results shown in Figure 6, where the lower curve has been calculated for a Stefan number three times as large as the real one. This is large enough to have a clearly defined region where z^* decreases with increasing flow rate.

Figure 7 shows the effect of varying the exit pressure (well outside of the region of practical interest). This, contrary to the effect of c_0, influences the LFA but not the HFA: raising the exit pressure is in a sense analogous to raising the feed mass fraction of polymer, in that in both cases the LFA and

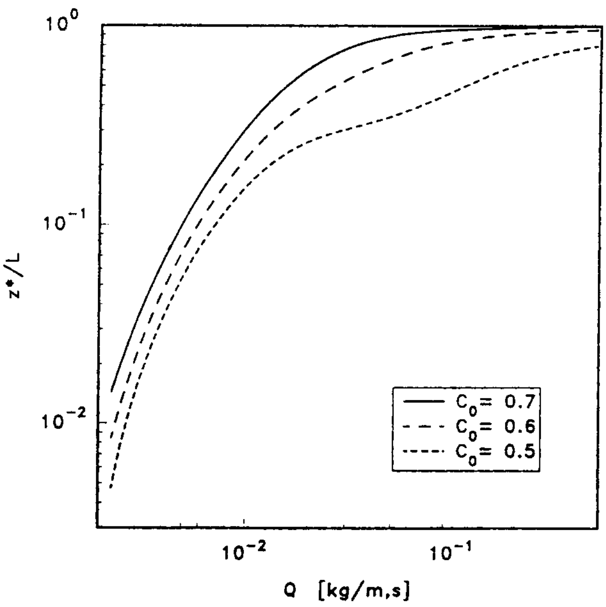

Figure 3. Axial position where the devolatilization starts, z^*, for three different values of the polymer concentration at the inlet.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $T_0 = 431$ K, $T_W = 533$ K).

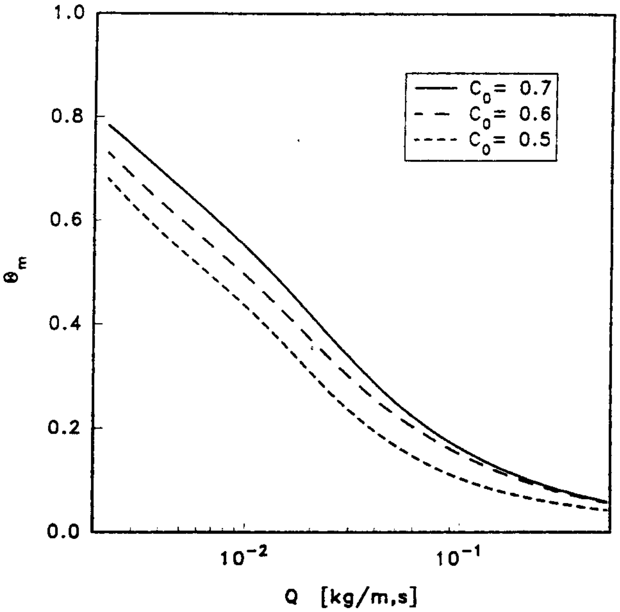

Figure 5. Dependence of the average temperature in the slit on the flow rate for three different values of the polymer concentration at the inlet.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $T_0 = 431$ K, $T_W = 533$ K).

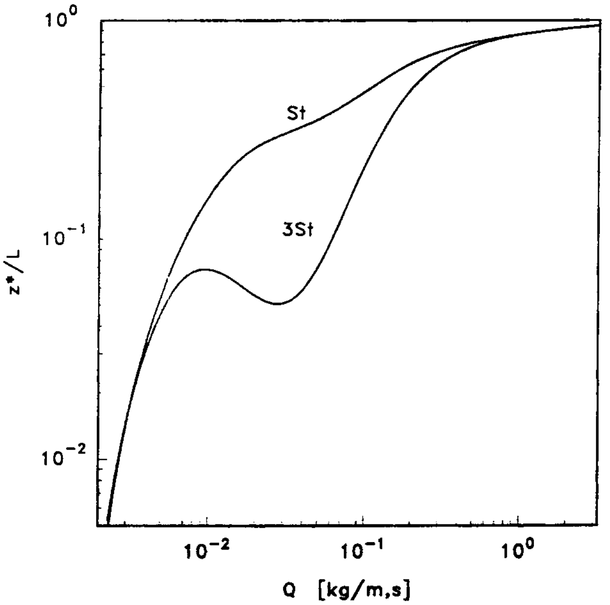

Figure 6. Axial position where the devolatilization starts for two different values of the Stefan number: the upper curve is the same plotted in Figure 3, the lower one is obtained with *St* three times greater.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $c_0 = 0.5$, $T_0 = 431$ K, $T_W = 533$ K).

the HFA get closer to each other. However, even at unrealistically high exit pressures the instability phenomenon has not disappeared.

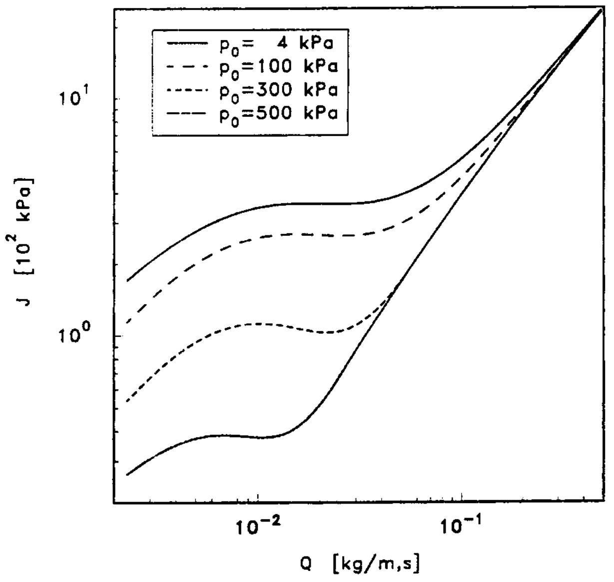

Figure 7. Dependence of the pressure drop in the slit on the flow rate for three different values of the pressure at the slit exit.

($A = 10^{-4}$ s/m, $c_0 = 0.6$, $T_0 = 431$ K, $T_W = 533$ K).

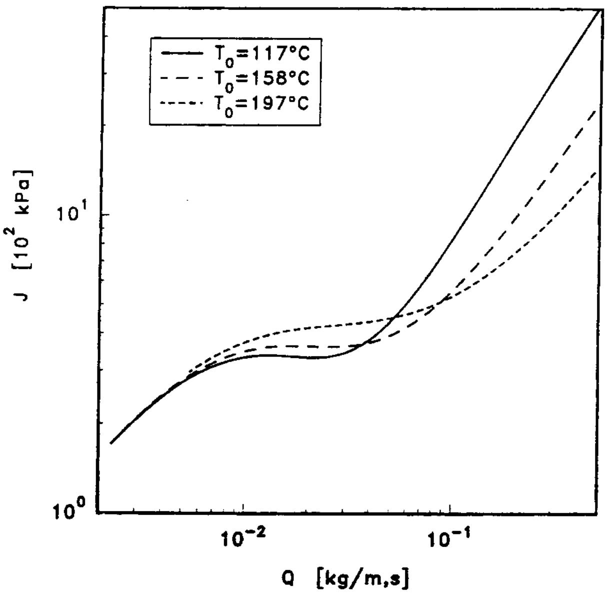

Figure 8. Dependence of the pressure drop in the slit on the flow rate for three different values of the solution temperature at the slit inlet.

($A = 10^{-4}$ s/m, $p_0 = 4$ kPa, $c_0 = 0.5$, $T_W = 533$ K).

Figure 8 presents the effect of varying the feed temperature to the slit. The LFA is of course independent of the feed temperature. Notice that at sufficiently high feed temperatures the instability phenomenon disappears. However, this is not a practical way of eliminating the problem. This multislit process has the main advantage of a low residence time of the polymer in the high-temperature region, so that thermal degradation is minimized; it follows that the feed should be at a temperature well below that of the devolatilization zone.

Effects of Rheology

Following Maffettone et al. (1991), the polymer phase has been regarded as a Newtonian fluid throughout the whole analysis presented above. Indeed, reliable viscosity data over the whole volatile concentration range of interest are available only for the zero-shear range, and therefore there is nothing better which can be done at this stage in a quantitative sense. However, a qualitative analysis of the effect of the non-Newtonian character of the polymer phase is useful.

As long as the flow rate Q is moderately small, the shear rates in the slit are low enough that the zero shear viscosity is likely to be a very good approximation. The largest shear rate is encountered at the wall, and (under the assumption of Newtonian behavior) it can be calculated from Eq. 5 to be $6P/\rho H^2$. At the largest flow rates corresponding to an acceptable level of devolatilization, this does not exceed about 10 s^{-1}, and this is well within the limits where the viscosity is still the zero shear one: data on the onset of shear thinning for the systems considered here are given by Mendelson (1979, 1980).

However, the minima of the curves in Figures 2, 6, 7 correspond to much higher flow rates, where the shear thinning effect is no longer negligible. Since the actual apparent viscosity is invariably smaller than the zero shear one, the actual high flow rate asymptote lies below the ones drawn in the Figures, and in fact it has a lower slope (equal to the power law index n). It follows that the actual minimum value of J is likely to be significantly less than the one calculated from our model equations. This leads to the conclusion that shear thinning results in a smaller range of stable operation of the multislit configuration than one would have should the polymer phase always behave as a Newtonian fluid.

Conclusions

Multislit devolatilization of polymers has been shown to be an inherently unstable operation, with flow rates per slit being quite different from each other in most situations where one tries to impose an average flow rate per slit comparable to the optimum one for single slit operation. A methodology for estimating the maximum flow rate per slit which is operable under stable conditions for a multislit system has been established. The influence of operating conditions on the stability problem has been considered. The effect of non-Newtonian properties of the feed solution on the stability problem has been discussed.

The main conclusion of this work is that heat transfer appears to be the controlling phenomenon. This is of interest because models of other devolatilization processes, which are available in the literature, mostly neglect the heat-transfer phenomenon altogether. The asymptotic analysis which has been presented implies that heat transfer is an important phenomenon whenever the feed value of the volatile mass fraction is not negligibly small.

Notation

A = mass-transfer coefficients, s/m
c = volatile mass fraction
c_G = gas specific heat, kcal/kg, K
c_P = liquid specific heat, kcal/kg, K
c_0 = feed value of c
E = dimensionless mass-transfer coefficient
$f(\ )$ = function delivering the volatile vapor pressure, kg/m·s^2
$F()$ = dimensionless form of $f(\ )$
G = gas mass flow rate per unit width, kg/m·s
Gz = Graetz number
h = gas layer thickness, m
H = slit thickness, m
J = pressure drop, kg/m·s^2
k = liquid thermal conductivity, kcal/m·s·K
K = a positive constant
$l(\ )$ = function of Q delivering J
L = slit length, m
m = local devolatilization rate, kg/m^3·s
m^* = average value of m, kg/m^3·s
N = number of slits
p = pressure, kg/m·s^2
p_0 = pressure at exit, kg/m·s^2
P = liquid mass flow rate per unit width, kg/m·s
q = heat flux, kcal/m^2·s
q_W = heat flux at the wall, kcal/m^2·s
Q = feed flow rate per unit width of slit, kg/m·s
Q_I = Q value corresponding to an intersection, kg/m·s
Q_T = total feed flow rate per unit width of slits, kg/m·s
r = dimensionless heat flux
r_W = value or r at the wall
St = Stefan number
T = liquid phase temperature, K
T_W = wall temperature, K
T_0 = feed temperature, K
T° = reference temperature, K
T^* = average temperature, K
u = x/H
U = dimensionless exit pressure
v = liquid phase axial velocity, m/s
w = P/Q
x = distance from wall, m
y = distance from inlet, m
z = y/L

Greek letters

β = p/p_0
γ = specific heat ratio
Γ = latent heat at reference temperature, kcal/kg
δc = change of c along the slit
δQ = displacement from steady flow rate, kg/m·s
$\delta \Theta$ = change of Θ along the slit
Θ = dimensionless temperature
Θ^* = average dimensionless temperature
μ = viscosity, kg/m·s
ρ = polymer density, kg/m^3
σ = dimensionless viscosity

Literature Cited

Astarita, G., and P. L. Maffettone, "Devolatilization of Polymers," *Adv. Transport Proc.*, **9**, in press (1992).

Brown, R., "Heat or Mass Transfer in a Fluid in Laminar Flow in a Circular or Flat Conduit," *AIChE J.*, **6**, 179 (1960).

Drew, T. B., "Mathematical Attacks on Forced Convection Problems: A Review," *Trans. AIChE*, **26**, 6 (1931).

Forsythe, G. E., and W. R. Wasow, *Finite-Difference Methods for Partial Differential Equations*, Wiley, New York (1960).

Ianniruberto, G., "Stabilita della Devolatilizzazione di Polimeri in Sistemi a Multifessura," Senior Thesis in Chemical Engineering, University of Naples (1992).

Lynn, S., and C. D. Oldershaw, "Analysis and Design of a Viscous-Flow Cooler," *Heat Transfer Eng.*, **5**, 86 (1982).

Maffettone, P. L., "Devolatilizzazione di Polimeri," PhD Thesis in Chemical Engineering, University of Naples, Italy (1993).

Maffettone, P. L., G. Astarita, L. Cori, L. Carnelli, and F. Balestri, "Slit Devolatilization of Polymers," *AIChE J.*, **37**, 724 (1991).

Mendelson, R. A., "A Method for Viscosity Measurements of Concentrated Polymer Solutions in Volatile Solvents at Elevated Temperatures," *J. Rheol.*, **23**, 545 (1979).

Mendelson, R. A., "Concentrated Solution Viscosity Behavior at Elevated Temperature-Polystyrene in Ethylbenzene," *J. Rheol.*, **24**, 765 (1980).

Nayfeh, A. H., *Perturbation Methods*, Wiley, New York (1973).

Shah, R. K., and A. L. London, *Laminar Flow Forced Convection in Ducts*, Academic Press, New York (1978).

Watson, K. M., "Thermodynamics of the Liquid State. Generalized Prediction of Properties," *Ind. Eng. Chem.*, **35**, 398 (1943).

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