The Pitot tube measurements are being compared directly with averaged water linear velocity measurements made with a hot film anemometer.

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NOTATION

A = cross-sectional area of pipe, m^2
C = calibration coefficient, Equation (1)
$<G>$ = cross section averaged mass velocity, kg/(m^{2}s)
$\overline{\Delta P}$ = arithmetic average of dynamic pressures measured by Pitot tubes, Pa
$<\rho>$ = cross section averaged mixture density, kg/m^3 $\frac{1}{A}\int_A \rho dA$
ρ = local mixture density, kg/m^3

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Comments on Polymerization of Styrene in a Tubular Reactor

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In a recent two-part paper, Wallis et al. (1975*a, b*) presented the results of an experimental investigation and a modeling study of the polymerization of styrene in a tubular reactor. From their work they concluded that a tubular reactor is a technically feasible replacement for a stirred-tank reactor for carrying out the first 30 to 40% of the polymerization. In this communication, a simple method is developed for estimating temperature and composition gradients in a tubular polymerizer. For the reasons outlined below, it does not appear that either the experimental work or the mathematical model of Wallis et al. justifies their conclusion.

Kwon (1976) pointed out the nature of the problem in qualitative terms, explaining that the higher residence time of the solution flowing near the wall, and the resulting increase of polymer concentration there, would result in a significant distortion of the velocity profile relative to the parabolic profile assumed by the authors. In his response, Wallis (1976) disagreed that this effect would be significant. Also relying on qualitative arguments, he maintained that the effect of a nonparabolic velocity profile on monomer conversion to polymer is small; that the combination of high shear stress at the wall and molecular diffusion would prevent a buildup of polymer near the wall; that no polymer buildup was observed when their reactor was dismantled; that the agreement between the experimental results and the predictions of the model justifies the assumed velocity profile; and that the duration of the experimental runs assured that steady state operation had been attained. Since this matter is of potential industrial interest, a more quantitative discussion would appear to be worthwhile.

The experimental reactor (Wallis et al., 1975*a*) had an inside diameter of 23.62 mm and a nominal length of 6.10 m. The method of operation was to feed styrene monomer to the reactor for a period of time equal to three average residence times, which varied from 4 309 to 9 569 s. Samples were then taken over a period of 1 800 s, after which the reactor was shut down and flushed with 2.5 times its volume of toluene. The authors did not reveal the reasoning by which three residence times were deemed to assure attainment of steady state operation.

For their mathematical model, Wallis et al. (1975*b*) used two equations of change of importance to this discussion. When x_m is defined as weight fraction monomer and R_p is expressed in terms of weight fraction, they become

$$V_{zo}\frac{\partial x_m}{\partial z} = -R_p + \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial x_m}{\partial r}\right) \qquad (1)$$

and

$$\rho_o C_p V_{zo}\frac{\partial T}{\partial z} = -\Delta H_r R_p + \frac{k}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) \qquad (2)$$

with boundary conditions

$$\frac{\partial x_m(0,z)}{\partial r} = \frac{\partial x_m(R,z)}{\partial r} = \frac{\partial T(0,z)}{\partial r} = 0$$

$$\text{and} \quad T(R,z) = T_w$$

The symbols, which are conventional, are listed in the notation.

Equivalent equations were previously presented by Lynn and Huff (1971) in a similar study of polymerization in a tubular reactor. However, there are important differences between the two papers in the assumptions which were made in order to integrate these equations. Wallis et al. (1975*b*) assumed that the polymer does not diffuse. This is inconsistent with their assumption that the density of the solution is a simple function of T and x_m. In fact, since the monomer and polymer together constitute the bulk of the solution, the diffusion process will be equivolume counterdiffusion, as required by the equation of continuity. The diffusional flux of monomer will thus produce a counterflux of polymer.

Of more importance to the present discussion, however, is the assumption regarding the velocity profile. Wallis et al. (1975*a, b*) assumed the profile to be parabolic, independent of the concentration profile. Lynn and Huff (1971) showed that if one neglects radial pressure gradients, the following expression is obtained:

$$\frac{V_z(r)}{\overline{V}_{zo}} = \frac{\rho_0 R^2 \displaystyle\int_R^r \frac{r}{\mu(r)}\,dr}{2\displaystyle\int_0^R \rho(r)\, r \int_R^r \frac{r}{\mu(r)}\,dr dr} \tag{3}$$

To evaluate this expression, one must know the viscosity and density profiles, which are obtained from the composition and temperature profiles and the relationships by which μ and ρ are related to x_m and T for the solution in question. It is appropriate to use the zero shear viscosity, since in most cases of interest the shear stress is quite low. Since the variation in density is small, to a first approximation, ρ may be assumed to be constant. Lynn and Huff (1971) studied a system in which the viscosity after polymerization was 170 times that of the feed. A gross distortion of the velocity profiles occurred near the front end of the reactor. Large temperature gradients were also found.

Wallis et al. (1975*b*) commented on this work, stating rather inaccurately that a relatively large tube diameter was used causing runaway reactions; that there was no correlation made between this behavior and either the tube diameter or the wall temperature; and that the effect on average monomer conversion and average molecular weights was not calculated. In fact, Lynn and Huff (1971) discussed the results of calculations for three different reactor diameters (18.8, 73.7, and 457 mm), the smallest being smaller than that used by Wallis et al. (1975*a*). The reactor walls were temperature-controlled in some cases and insulated in others. Monomer conversion as a function of radial position and axial distance was presented graphically for seven different cases. Tabulations of both molecular weights and molecular weight distributions for various products were given. In addition, a method was discussed for preventing severe distortion of the velocity profiles. It was shown that adding polymer to the feed (by any of several ways), so that the change in viscosity within the reactor was reduced to a factor of about 30 or less, reduced velocity distortion to the point where it would no longer be of concern.

In the case of styrene-polystyrene solutions, the viscosity increases by about a factor of 10 for each increase of 0.1 wt fraction polymer (Boundy et al., 1970). Thus, to avoid severe velocity distortion, one would want to have a radial variation of x_m no greater than 0.15 at any axial position in a tubular reactor. Similarly, Wallis et al. (1975*b*) stated that the radial temperature variation should be kept below 15°C. Under conditions of nearly constant composition and temperature, to a first approximation, the rate of polymerization R_p would be about constant at any axial position. A consideration of Equations (1) and (2) shows, however, that this radial constancy of x_m and T could only persist along the tube if the terms on the left-hand side of the two equations were small relative to those on the right. Thus, to obtain small radial gradients one must be able to assume that the process of molecular diffusion prevents the development of large concentration gradients due to the velocity profile and that thermal diffusion transports the heat of reaction to the wall. It is instructive to take the data for a typical experiment to see if these assumptions are, in fact, reasonable.

The data of Experiment 4 (Wallis et al., 1975*a*) are typical of the experimental work presented. Wall temperature was 80°C, residence time was 8 032 s, average conversion was 27.8%. The average rate of polymerization R_p was thus $3.46 \times 10^{-5}\,\text{s}^{-1}$. When one makes the assumptions above, Equation (2) becomes

$$\frac{k}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = \Delta H_r R_p \tag{4}$$

The boundary conditions remain the same. Integrating twice, one obtains

$$T_0 - T_R = \frac{-\Delta H_r R_p}{4k} R^2 \tag{5}$$

From the values given by Wallis et al. (1975*b*) for ΔH_r and k, -160 cal/g and 3×10^{-4} cal/cm²-g-°C, and 1.18 cm for R, $\Delta T = 6.42$°C. This value is about one third of the maximum ΔT presented in their Figure 1 by Wallis et al. (1975*b*) if one interpolates to the condition for Experiment 4. That much difference is to be expected between the maximum value of R_p and the average value used here. Their conclusion that radial temperature variations were moderate is thus supported by this calculation.

The composition profile of monomer for this tubular reactor will always be sigmoid in shape, with zero gradients at the center line and wall. In the central region there is a diffusional flux out that supplies the material that is polymerizing in the annular region near the wall. Defining the boundary between these two regions as r_a, the location of the point of inflection in the composition profile, one obtains the following two equations from Equation (1):

$$\frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial x_m}{\partial r}\right) = -R_p\left[\frac{(R^2 - r_a^2)}{r_a^2}\right] \qquad 0 \leqq r < r_a \tag{6}$$

and

$$\frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial x_m}{\partial r}\right) = R_p \qquad r_a < r \leqq R \tag{7}$$

Let it be assumed that at r_a the velocity is always the same as the average velocity of the solution in the reactor; that is, that the point of inflection of the composition profile always coincides with the point at which $V_z = \overline{V}_z$. It would follow that the value of x_{m,r_a} at any axial position would be the value it would have in a plug flow reactor. The profiles presented by Lynn and Huff (1971) show that this assumption is not greatly in error. The smaller the radial variation in composition is, the less important any error involved in this assumption will be.

Integrating the two equations, one obtains

$$x_{m,0} - x_{m,r_a} = \frac{R_p R^2}{4D}\left(1 - \frac{r_a^2}{R^2}\right) \tag{8}$$

and

$$x_{m,r_a} - x_{m,R} = \frac{R_p R^2}{4D}\left[\left(\frac{r_a^2}{R^2} - 1\right) + 2\ln\frac{R}{r_a}\right] \tag{9}$$

The value obtained for $\partial x_m/\partial r$ at r_a is the same for both regions. Adding Equations (8) and (9), we get

$$x_{m,0} - x_{m,R} = \frac{R_p R^2}{2D}\ln\frac{R}{r_a} \tag{10}$$

For a parabolic velocity profile, $r_a/R = 1/\sqrt{2} = 0.707$. The value of D assumed by Wallis et al. (1975*b*) is 2×10^{-5} cm^2/s. Thus, $\Delta x_m = 0.417$. This value is greater by about a factor of 3 than the value which may obtain without causing severe flow distortion. The effect of such distortion would be to decrease r_a, further increasing the value calculated for Δx_m. The value taken for D is, if in error, larger than that which would be expected for this system. It is clear that with such a large radial variation in x_m, one could not in fact have a constant value of R_p. However, the point of this calculation is to show that molecular diffusion could not have prevented the development of a large radial gradient in x_m in a tubular reactor under the conditions which prevailed in the experimental part of their work.

It must therefore be concluded that the model proposed by Wallis et al. (1975*b*), which assumes a parabolic velocity profile for the entire length of the reactor, is seriously in error. At steady state, a large fraction of the tube would be occupied by very slowly moving polymer, and the bulk of the solution would flow rapidly through a small hole down the center line, to emerge nearly unreacted because of the short residence time. The only alternative is to assume that natural convection, due to density gradients resulting from temperature of composition differences, is sufficient to produce, uniformly throughout the tube, an effective diffusivity at least four times the molecular diffusivity. This assumption seems unlikely. It must be pointed out that the shear gradient does not produce radial motion in laminar flow and cannot be proposed as a mechanism for moving polymer away from the wall.

The model proposed by Wallis et al., (1975*b*) would clearly predict a higher conversion of the monomer flowing near the wall than of that near the center. As a result, they found better agreement with their experimental data in predicting conversions and molecular weights with this model than with a plug flow model. It would be logically inconsistent to argue that this radial variation in composition is meaningful when used to predict conversions but of no significance in determining the velocity profile. In choosing to assume a parabolic velocity profile, Wallis et al. (1975*b*) appear to have been unaware of the extent of the distortion which might occur. There is no indication that velocity profiles were calculated, using Equation (3), to check their assumption.

In view of the calculation above of the composition difference which would obtain at steady state, it seems highly unlikely that steady state was achieved during the experiments reported by Wallis et al. (1975*a*). Even if a parabolic velocity profile had obtained, it would follow that the outer 19% of the reactor volume (where r is greater than 0.9 R) would have been occupied by solution flowing with an average velocity of only about 0.1 $\overline{V}_z$. The average steady state residence time of this sheath would thus have been about ten times the average residence time of the solution as a whole. Since the duration of these experiments was of the order of only 3.4 times the average residence time, there is no way that the material in the outer sheath could have reached steady state. The fact that no polymer buildup was observed is simply the result of the clean-up procedure which was followed after each experiment. What they failed to realize is that a similar cleanup procedure, repeated at approximately 8 hr intervals, would be required if a similar tubular reactor were to be operated commercially.

It appears that Wallis et al. (1975*b*) made the common, but dangerous, assumption that reasonable agreement between their model and their experiments demonstrated the validity of both. Unfortunately, the parameters they chose to compare, conversions and molecular weights, are rather insensitive to flow model. This is demonstrated by the fact that the predictions based on their plug flow model differ by only 4% from those based on the parabolic profile. The 2% difference between the latter and their experimental results cannot, therefore, be taken as an indication that the parabolic profile is justified.

In summary, it must be concluded that a tubular reactor in laminar flow will most probably be technically infeasible as a reactor for the polymerization of styrene. The reason is the distortion in velocity profile which develops, and the large variation in residence time which results therefrom. The contrary conclusion of Wallis et al. (1975*a*, *b*) was based on a misinterpretation of their experimental work and a poorly designed mathematical model.

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NOTATION

C_p = heat capacity
D = diffusion coefficient
k = thermal conductivity
r = radial distance from center line
R = radius of tubular reactor
R_p = rate of polymerization
T = temperature
T_w = wall temperature
V_z = velocity of reacting stream (varies with r)
$\overline{V}_o$ = average velocity of stream at inlet
$\overline{V}_z$ = average velocity of stream at axial position z
x_m = weight fraction monomer
z = axial distance from reactor inlet

Subscripts

μ = viscosity
ρ = density

Greek Letters

o = inlet
0 = center line
R = wall

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