LETTERS TO THE EDITOR

TO THE EDITOR:

The reactors discussed in the articles by Wallis, et. al. *Continuous Production of Polystyrene in a tubular reactor, Part I and Part II [AIChE J.,* **21** (4), 686-698 (1975)] are interesting in that, if the reactor of this type is successfully realized for industrial processes, it could lead to considerable economization of the process for bulk polymerization of styrene.

However, there is one critical point which should be considered in achieving this realization and this was not clarified by the authors. The point is how the increase of shear viscosity with conversion of monomer to polymer would affect the velocity profile of reactant flow through the tube. The authors assumed a parabolic velocity profile (line 8, p. 693), but then the question is: would it remain parabolic? For the sake of discussion, let us start with a parabolic profile. The flow is obviously laminar in the authors' experiments and the monomer flowing near the wall would have a much larger residence time than the monomer flowing through the center. Thus, it will convert more to polymer and, consequently, its viscosity would be higher. This would result in a slowing of flow near the wall and pushing the reactant to the center. In the monomer—polymer bulk mixture, shear viscosity rises very fast with the increase of polymer fraction and this would worsen the situation furthermore. The authors also assumed no diffusion of polymer. Then, what would counteract the build-up of high-viscosity reactant layer along the wall? This high-viscosity layer could keep growing until the increased shear rate due to the decrease of effectively available cross-sectional area for flow would check any further growth of the layer.

In order for a better understanding of this point under the circumstance, it would be necessary to introduce a flow equation and account for the effect of viscosity increase on the velocity profile and, in turn, the effect of velocity profile on the radial profile of polymer fraction.

The authors assumed that a steady state would be reached in approximately three residence times which correspond to about 7 hours (p. 687). At 90°C, thermal polymerization of styrene in bulk proceeds at a rate of approximately 1% per hour in the beginning of reaction starting with pure styrene (Boundy and Boyer, 1952). If the effect of polymer build-up along the wall is to be seen, then, one should allow at least 100 hours and, in order to determine whether a steady state has been reached, the average conversion at the exit of tube should be observed as a function of time to see if it has leveled off to a steady value.

If only about 7 hours were allowed for reaching a steady state and if Eq. (22)-(25) were used without accounting for the change in the velocity profile from the parabolic profile due to the increase of viscosity with conversion, then the conclusions from the results could be seriously misleading.

LITERATURE CITED

Boundy, R. H. and R. F. Boyer, "Styrene, Its Polymers, Copolymers and Derivatives," Reinhold, New York, 1952.

Wallis, J. P. A., R. A. Ritter and H. Andre, "Continuous Production of Polystyrene in a Tubular Reactor," Part I, AIChE J., *21* (4), 686 (1975), Part II, AIChE J., *21* (4), 691 (1975).

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TO THE EDITOR:

Dr. Kwon has raised some relevant points on our papers titled "Continuous Production of Polystyrene in a Tubular Reactor".

First, the effect of a non-parabolic velocity profile on monomer conversion to polymer is small even for moderately distorted profiles. This has been pointed out on page 692, in particular paragraph 4, of our paper. Since we used a relatively small diameter tube the distortion would be minimal under the operating conditions used.

One would not expect polymer to build-up on the tubular reactor wall. The shear stress is greatest at the tube wall and lowest at the tube centre. The high shear stress coupled with monomer and polymer diffusion should ensure that polymer does not build-up on the wall. It is of course possible to "bake on" the polymer by having a hot wall temperature. This would not be conducive to achieving a good polymer product, which was the objective of our study. Our polymerization, initiated by AIBN, has been undertaken with cool-moderate wall temperatures ensuring that polymer would not be "baked on".

When the reactor was dismantled there was no evidence of polymer build-up on the reactor wall. Earlier work by Whitfield (G. St. Q. Whitfield, "The Continuous Production of Polyisoprene," Ph.D. Thesis in Chemical Engineering, University of Calgary, 1970), on isoprene polymerization initiated by N-butyl—lithium in an annular reactor, did not encounter any polymer build-up. His reactor showed no evidence of polymer build-up when it was dismantled.

Contrast this with a stirred tank reactor where the centre region is under a high shear and the reactor wall is under a very low shear stress. Polymer does build-up in reactors of this type. Consequently they are shut-down periodically for cleaning.

Our model neglects polymer diffusion, but the reactants polymerize and diffuse regardless of our assumptions. Since polymer does not cake to the tube wall and the model-experimental results agree, it appears that this simplifying assumption is valid. The objective is to match a simple model to the observed facts.

Since our system was AIBN initiated the polymerization reached steady-state very quickly. Reactor operation for at least seven hours (3 or more residence times) allowed sufficient purge time for concentration and temperature distributions along the reactor length and radius to become time independent. Thermal polymerization although small has been accounted for in the model. Consequently our results still remain valid even for long operation times.

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TO THE EDITOR:

Yu and Douglas (1975) have published, for application to a continuous crystallizer, a procedure for estimating the amplitude of a limit cycle that has been used in several earlier publications by Douglas and his co-workers. Acknowledging that the procedure gives qualitatively wrong conclusions about the character of the system in some cases, the authors explain that this problem arises because the procedure uses truncated Taylor expansions of certain functions appearing in the description of the system and that these truncated expansions do not give a correct topological description of the system in the large. Among the references they give to support this argument appears a reference to my paper of 1972.

This letter is written to point out that my paper does not support the position of the authors on this question, but explicitly opposes it. This is made clear by quoting one sentence, referring to a paper by Gaitonde and Douglas (1969): "The authors have overlooked the fact that the truncated expansion has significance only in the neighborhood of the origin of the expansion, so that its behavior in the large is irrelevant."

The real cause of the difficulty is the fallacy in the procedure used in this and earlier publications. It involves introducing a factor which is treated as arbitrarily small and also as being equal to unity. The failure of the method is demonstrated by its application to the system

$$\frac{dx}{dt} = 2\alpha x - y + 3x^2 - 3xy + \frac{1}{3}x^3$$

$$\frac{dy}{dt} = x$$

Here there is no question of Taylor expansions, and the only singular point is at the origin. The characteristic values of the linearized system are $\alpha \pm i\beta$, where $\beta = (1 - \alpha^2)^{1/2}$. After the transformation $x = u$, $y = \alpha u + \beta v$, the system is in the correct canonical form, and the procedure in question may be applied. It is worth noting that in the first approximation the procedure permits no contribution from the second-degree powers and products. The calculated value of the amplitude of the limit cycle in the first approximation is $(-8\alpha)^{1/2}$, which leads to the conclusion that no small limit cycle exists when α has a small positive value. The expressions given by Beek (1972), on the other hand, give the qualitatively different result $\alpha^{1/2} + \alpha + 0(\alpha^{3/2})$.

The validity of these results may be tested empirically by numerical calculation. The equations were integrated between two successive intersections of the trajectory in the phase plane with the positive x axis. The table shows x_o, the initial value of x, and $x_1 - x_o$, the corresponding change in x in the integration. A very small value of α, 4×10^{-6}, was used to provide a check on the accuracy of the analytically calculated amplitude, which is 2.004×10^{-3} in this case.

$10^3 x_o$	$10^8(x_1 - x_o)$
1.004	1.8906
2.004	−0.0092
3.004	−9.0494

These numerical results show that the system actually has a small limit cycle when α has a small positive value.

I am glad to acknowledge the generous permission of the staff of the Zeeman Laboratory of the University of Amsterdam to use the Laboratory's C.D.C. 6400 for the calculations.

LITERATURE CITED

Yu, K. M., and J. M. Douglas, "Self-generated Oscillations in Continuous Crystallizers: Part 1. Analytical Predictions of the Oscillating Output," *AIChE J.*, **21**, 917 (1975).

Beek, John, "Small Oscillations in Undistributed Autonomous Systems," *AIChE J.*, **18**, 228 (1972).

Gaitonde, N. Y., and J. M. Douglas, "The Use of Positive Feedback Control Systems to Improve Reactor Performance," *AIChE J.*, **15**, 902 (1969).

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TO THE EDITOR:

We believe that there is a fundamental error at an early stage in a paper by G. Grossman ["Stresses and Friction Forces in Moving Packed Beds," *AIChE Journal* 21, 720 (1975)] that completely negates the subsequent conclusions. The error appears in the footnotes to pages 723 and 724. The former, which states that "The column and flow are clearly symmetrical with respect to the y-axis," implies a sign convention for shear stress that introduces the singularity mentioned in the second footnote. In fact the shear stress distribution is antisymmetric about the y-axis and $\partial\tau/\partial x$ cannot be taken as zero below the Rankine zone. This then invalidates the centre-line boundary conditions, viz. (16) $\sigma = y/(1 + \sin\delta)$ and (18) $\sigma_y = y$. A sufficient boundary condition for the method of characteristics is merely the other part of (16), i.e. $\psi = 0$.

The analogy with Poiseuille flow between parallel planes is helpful in this context. Again the flow is clearly symmetrical, but the strain rate, $\partial v/\partial x$, and hence the shear stress, is antisymmetric and $\partial\tau/\partial x \neq 0$ on the y-axis.

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TO THE EDITOR:

I have checked the points raised in the letter from Professors Horne and Nedderman and I agree completely. There is an error in the center line boundary condition (16) and (18) stating that at $x = 0$ $\sigma y = y$. While this boundary condition is valid in zone 1 along the line OB, it does not hold below. This error results from the wrong impression that along the center line where $\partial\tau/\partial x$ changes sign in the presently used coordinate system, one can use $\partial\sigma y/\partial y = 1$ for symmetry arguments which is equivalent to setting $\partial\tau/\partial x = 0$ in equation (12). $\partial\tau/\partial x$ itself *was not* assumed zero on the center line as shown in Figure (3c) and equation (23).

I also agree that in equation (16) $\psi = 0$ on the center line is a sufficient boundary condition for the method of characteristics. This is in fact the way equations (14) and (15) had been solved, without the additional condition $\sigma = y/(1 + \sin\delta)$. What surprises me is the good agreement between this solution and the one obtained by the integral method (Fig. 5) which now turns out to be incorrect. I intend to revise the integral solution and compare it again with the exact one by the method of characteristics.

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ERRATA

The article "Constitutive Equation for Vapor Drift Velocity in Two-phase Annular Flow" by Mamoru Ishii, T. C. Chawla, and N. Zuber (*AIChE J.*, Vol. 22, No. 2, 283-289, 1976) has errors in Figures 1 and 2. The numbers of Equations in the Figures should read, respectively, Eqs. (28), (29), (30), (32), (33), and (35) instead of Eqs. (21), (22), (23), (25), (26), and (28).