Part II. Non-Newtonian Fluids

The laminar flow of dilute aqueous polymer solutions was studied in the entrance region of a cylindrical tube. In laminar, fully developed, steady tube flow, elastic and inelastic fluids were indistinguishable. Viscoelastic fluids exhibited much higher entrance pressure losses than did inelastic fluids with comparable viscous properties. A method has been developed for separating the elastic portion of the overall entrance loss and shows that in some cases the elastic contribution represents as much as 80% of the total. An analysis is also presented which allows calculation of the elastic entrance loss in terms of a Hookean shear modulus.

The first paper of this series discussed the entrance-region flow of Newtonian fluids (*26*). This work extends the analysis to non-Newtonian fluids.

Two categories of non-Newtonian fluids may be envisioned: inelastic and viscoelastic. In the former, despite a nonlinear, shear stress vs. shear rate relation, all applied mechanical energy is dissipated through viscous friction, while in the latter a portion of the energy is stored elastically when the fluid is in a stress field (*11, 14, 18, 27*). It would be expected that this elastic energy storage would cause an increased excess entrance pressure loss over and above that caused by a fluid's purely viscous characteristics. In other words, two fluids having the same shear stress-shear rate behavior in steady, laminar flow, but characterized by different elastic properties, may present different values of ΔP_{ent}. The implication of Bird (*4*) that no two such fluids may exist has been discussed (*1*); in fact, liquids do exist which exhibit a Newtonian flow behavior, yet are elastic in character (*13*).

For an inelastic fluid whose shear properties are adequately represented by the power law (*24*)

$$g_c\,\tau = K_p\,\dot{\gamma}^{\,n} \qquad (1)$$

dimensional considerations show that (*25*)

$$g_c\frac{\Delta P_{\text{ent}}}{\frac{1}{2}\rho V^2} = f\,(N_{Re},\,\beta,\,n) \qquad (2)$$

If the function in Equation (2) is to be written in the form shown to be valid for Newtonian fluids (*26*)

$$g_c\frac{\Delta P_{\text{ent}}}{\frac{1}{2}\rho V^2} = K + K'/N_{Re} \qquad (3)$$

then both K and K' must be functions of n as well as β.

Entrance analyses similar to those for Newtonian fluids have been given by Bogue (*5*) and Collins and Schowalter (*9*) for purely viscous power law fluids. In both cases it was found that K decreased with decreasing n. There are really no concrete theoretical analyses concerning the entrance-region flow of viscoelastic fluids, although a few qualitative boundary-layer analyses have been published (*12, 17*). For viscoelastic fluids, there are presumably one or more dimensionless groups in addition to N_{Re}, β, and n which are necessary to characterize $g_c\frac{\Delta P_{\text{ent}}}{\frac{1}{2}\rho V^2}$. The questions are what are they and how might they be determined?

Bogue and Doughty (*6*) have reviewed a number of constitutive equations and discussed the formation of dimensionless groups. For constitutive theories involving a time derivative of stress [Oldroyd type (*19*)] and those involving an integrated deformation history [Coleman and Noll type (*7*)], they found a dimensionless time constant similar to the Deborah number. The Deborah number, explicitly discussed by Reiner (*23*) and treated in a more quantitative manner by Metzner, White, and Denn (*16*), is the ratio of the characteristic time of the fluid to the characteristic time of the process. However, for cases such as this, where equilibrium flow is reached for all practical purposes (Deborah numbers approaching zero), it would be of little significance even if it could be evaluated quantitatively for a given fluid under a given set of conditions. It is also tempting to try to relate elastic effects to the normal stress coefficients, but it must be kept in mind that the latter are defined only for viscometric flows (*8*), and flow in the entrance region is most definitely not viscometric. The ultimate answer would be solutions to the equations of motion using appropriate constitutive relations, but in view of the lack of general success with the simplest (Newtonian) constitutive equation, for the time being, other means must be developed to demonstrate and characterize elastic contributions to the entrance pressure loss.

EXPERIMENTAL

The experimental setup and procedures have been described previously (*26*). Test fluids were aqueous solutions of carboxy methylcellulose (CMC), poly (ethylene oxide) (Polyox) and poly (acrylamide) (Separan). Because of the sensitivity of the polymers to mechanical degradation, before any data are obtained, the solutions must be circulated for long periods of time, 24 hr. or more, until the viscosities measured in the Ubbelohde viscometer had stabilized. Periodic checks were made during the runs to be sure that degradation had ceased. Degradation was particularly severe in the case of the Polyox solutions.

RESULTS

Flow curves for some of the experimental fluids are

TABLE 1. POLYMER SOLUTION PROPERTIES

Polymer (code name)	Concentration, wt. %	$\frac{K_p}{g_c} \times 10^4$, lb.$_f$sec.^{n}/in.^{2}	n, dimensionless
P-301 (P-A-4)	2.27	8.27	0.433
P-301 (P-A-5)	2.90	14.9	0.413
P-301 (P-A-6)	3.70	30.1	0.382
P-301 (P-B-1)	1.34	1.56	0.523
P-301 (P-B-2)	2.15	3.79	0.478
CMC-7H(CMC-1)	0.83	2.59	0.505
CMC-7H(CMC-2)	1.376	11.76	0.395
Separan (S-1)	0.68	1.67	0.462
Separan (S-2)	1.10	5.48	0.365
Separan (S-3)	1.65	9.0	0.356
Separan (S-4)	2.20	20.6	0.289

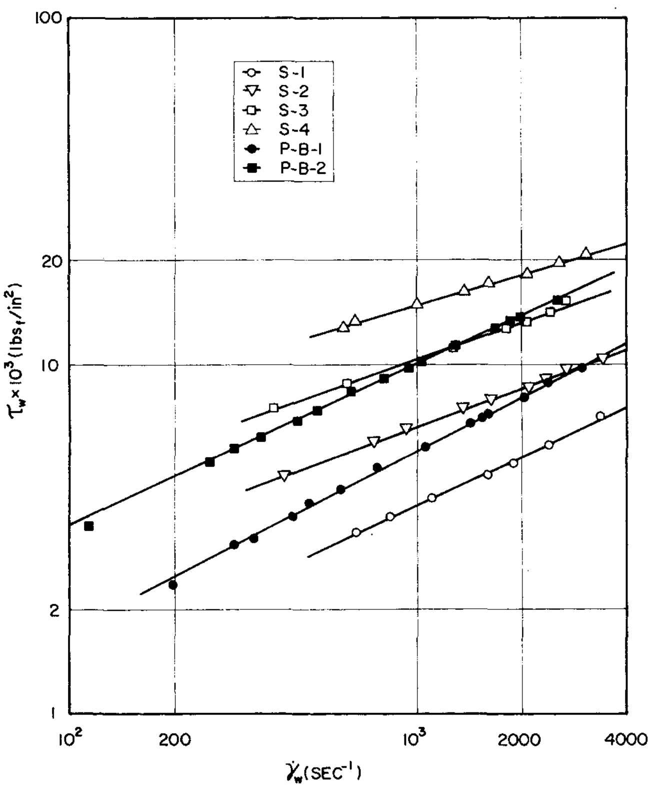

Fig. 1. Representative flow curves.

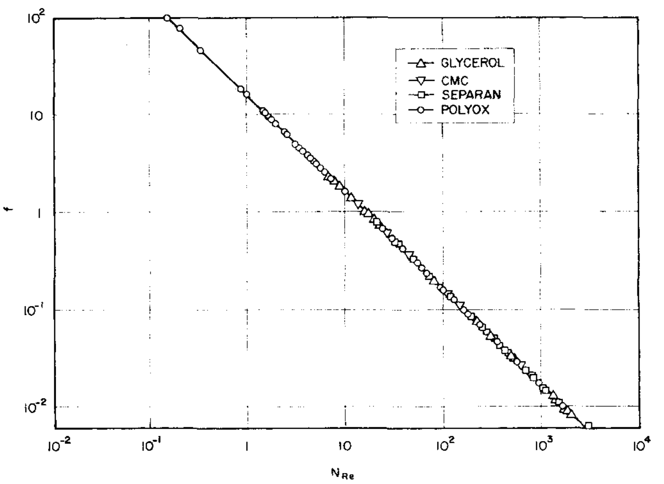

Fig. 2. Friction factor vs. Reynolds number, calculated from the equilibrium pressure gradients.

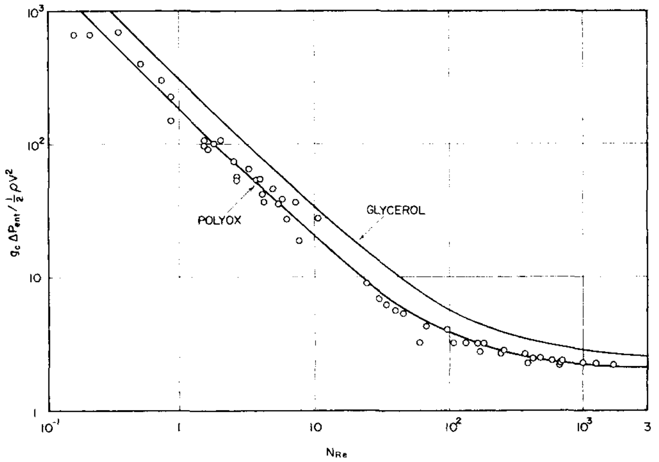

Fig. 3. Dimensionless entrance loss vs. Reynolds number for Polyox solutions.

shown in Figure 1. These were calculated from the true equilibrium pressure gradient $(\partial P/\partial x)$. The power law is an excellent approximation for all the fluids over the range of shear rates studied. The concentrations and power law constants of the various test fluids are given in Table 1.

While the pressure profiles were qualitatively similar to those observed for Newtonian fluids, larger entrance losses were immediately evident in many cases, and in only one instance was any evidence for a vena contracta observed, solution PB-1 at $N_{Re} = 1{,}633$ (the highest attained). This is attributed to the value of n for this solution (the largest of any of the polymer solutions) and to the relatively low elastic losses (to be demonstrated later) for the Polyox solutions. Lower n's result in flatter velocity profiles both upstream and downstream, requiring less rearrangement through the contraction, and are thus expected to suppress vena contracta formation. Also, the large entrance losses for the viscoelastic solutions probably masked the vena contracta, if present.

Since the extrapolated pressures at the tube exit plane were invariably zero (gauge) within the limits of experimental precision (± 0.01 lb./sq.in.), normal stresses and any tap hole effects, if present, were too small to influence the experimental determination of ΔP_{ent}.

A friction factor vs. Reynolds number plot showing representative data for all test fluids, including the Newtonian, is given in Figure 2. All values were calculated by using (*24*)

$$N_{Re} = \frac{\rho\, D^n\, V^{2-n}}{K_p\, 8^{n-1} \left(\dfrac{3n+1}{4n} \right)^n} \tag{4}$$

$$f = g_c \frac{D}{4} \left(\frac{\partial P}{\partial x} \right) \Big/ \frac{\rho V^2}{2} \tag{5}$$

For Newtonian fluids, $n = 1$, Equation (4) reduces to the usual Reynolds number. The line drawn is not fitted to the data but is the conventional relation $f = 16/N_{Re}$.

Metzner and Reed (*15*) considered a variety of non-Newtonian data and found that it could be summarized fairly well by $f = 16/N_{Re}$ for $N_{Re} < 2{,}100$. However, this is the first time that extensive laminar $f - N_{Re}$ data have been obtained for fluids which are clearly elastic. They prove conclusively that in steady, fully developed laminar flow, fluid elasticity is of no consequence whatsoever. This of course is not true in other situations, for example, in turbulent flow, where the phenomenon of drag reduction is well documented, and in the entrance region (as will be demonstrated). In both these cases, fluids with similar viscous properties can exhibit significantly different flow behavior. It should be pointed out that when the total pressure drop from reservoir to tube exit was used to calculate f, errors as large as 80% were obtained, despite the tube L/D of 192. This could be of serious consequence in the design and analysis of data from capillary viscometers.

Figure 3 is a plot of dimensionless entrance pressure drop vs. Reynolds number for the Polyox solutions. As was the case for the Newtonian fluids, the data are in good agreement with Equation (3) over four decades of N_{Re}, with $K = 2.1 \pm 0.1$ and $K' = 185 \pm 25$. No great distinction between the various concentrations is apparent.

The Newtonian curve is included for comparison. The Polyox data fall well below it, as would be expected for fluids with smaller n.

In Figure 4, the data for the Separan and CMC solutions are compared with the results for the Polyox. It is immediately apparent that over the entire range of Reynolds numbers, the dimensionless entrance losses are appreciably greater for Separan and CMC than for Polyox, despite the fact that the various solutions had similar n's. In fact, the $g_c \, \Delta P_{ent} / \frac{1}{2} \rho V^2$ data for Separan and CMC are comparable to or greater than those for the Newtonian fluids, again despite their smaller n's, which alone should cause lower entrance losses. These observations can only be explained by the presence of large elastic contributions to the entrance loss in the case of the Separan and CMC solutions, much larger than those exhibited by the Polyox solutions. Aqueous solutions of poly (ethylene oxide) are normally considered highly elastic in a qualitative sense. The quantitative observations above may result, in part, from the severe degradation of these solutions in the flow system before data were taken.

It is now fairly clear why no great distinctions in entrance losses are observed for the various concentrations of polymers. Solution elasticity would be expected to increase with polymer concentration, raising entrance losses. This rise is compensated by the decrease in n with increased concentration, which lowers entrance losses.

It has been shown that fluids with similar viscous properties can exhibit significant differences in entrance losses which must, in some fashion, be attributable to fluid elasticity. It would be useful to be able to separate this elastic contribution to the entrance loss. To this end, we introduce the working hypothesis that the Polyox solutions may be treated as inelastic (purely viscous) non-Newtonian fluids. This obviously is an oversimplification, but it is justified on the grounds of the much lower entrance losses observed for these fluids than for the solutions of the other polymers with similar equilibrium viscous properties. This, assuming an average $n = 0.4$ for all the Polyox solutions, together with the data for Newtonian fluids, fixes two points on the K and K' vs. n relations (at constant β): $K(n = 1) = 2.4$; $K(n = 0.4) = 2.1$; $K'(n = 1) = 295$, $K'(n = 0.4) = 185$. Then by using a linear relation between the constants and n (in lieu of other quantitative information), $K(n)$ and $K'(n)$ may be estimated and used with Equation (3) to calculate the purely viscous contribution to the entrance pressure loss. The validity of this technique is illustrated in Figure 5 in which $g_c \dfrac{\Delta P_{ent}}{\frac{1}{2}\rho V^2}$ is plotted against $K(n) + K'(n)/N_{Re}$. The line drawn represents perfect equality and is essentially coincident with the best-fit line through the data; it will henceforth be termed the purely viscous line. It is felt that at least some of the scatter is due to the assumptions involved, that is, inelasticity of the Polyox solutions, the use of an average n to represent all of them, and linear relations between the constants and n.

Figure 6 compares the data for the Separan and CMC solutions to the purely viscous line. There is no question as to the experimental or statistical significance of the differences. By subtracting the purely viscous values from the experimental ordinates, the elastic contributions to the total entrance loss are obtained. Values of the elastic entrance loss so calculated range from 20 to 80% of the total entrance loss.

In a recent article (*2*), Astarita and co-workers concluded that there were no conspicuous elastic effects on entrance losses in the laminar flow of non-Newtonian fluids. This is due to the fact that the opposing effects of n and elasticity on ΔP_{ent} were not recognized and separated. Figure 3 of reference 2 supports the conclusions presented here. In the absence of elasticity, all K' values should be less than those for Newtonian fluids, but elasticity has resulted in some being greater. The work of Feig (*10*) and Pruitt and Crawford (*22*) also indicate that viscoelastic liquids exhibit larger values of ΔP_{ent} than inelastic non-Newtonians.

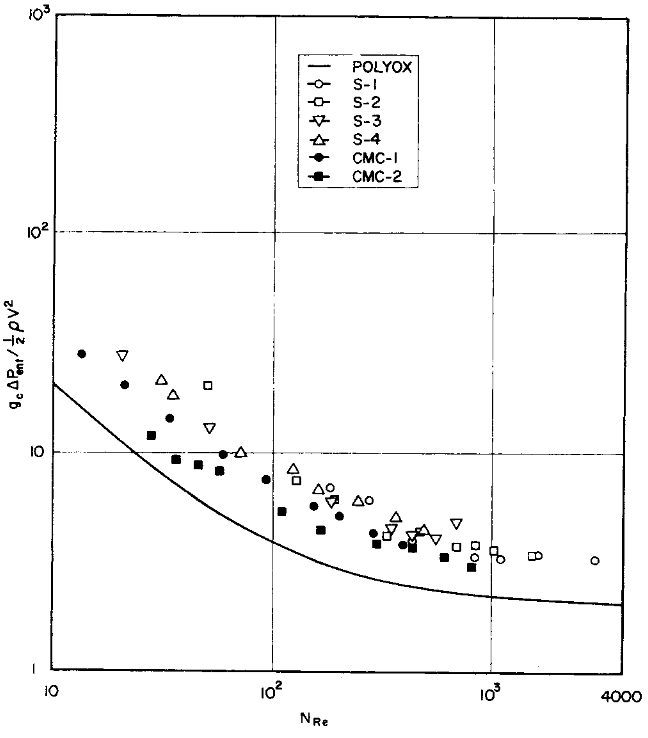

Fig. 4. Dimensionless entrance loss for Separan and CMC solutions compared with that for Polyox solutions.

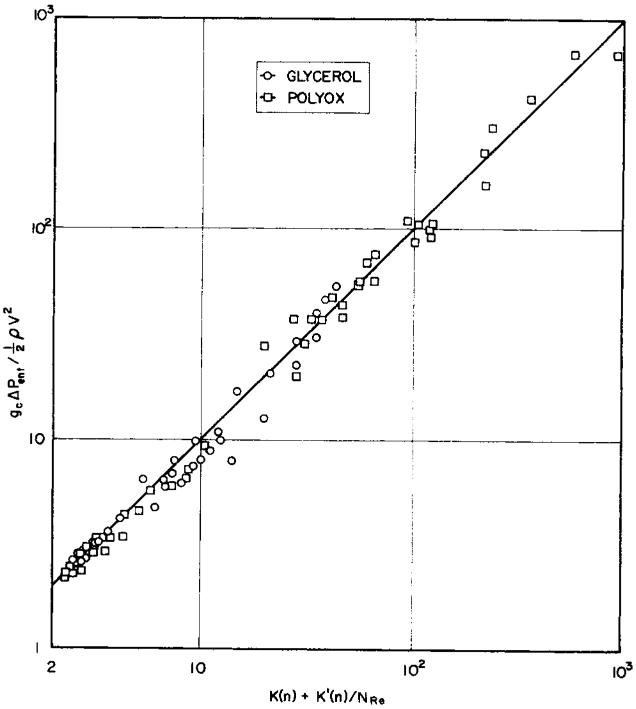

Fig. 5. Total dimensionless entrance loss vs. purely viscous contribution for glycerol and Polyox solutions.

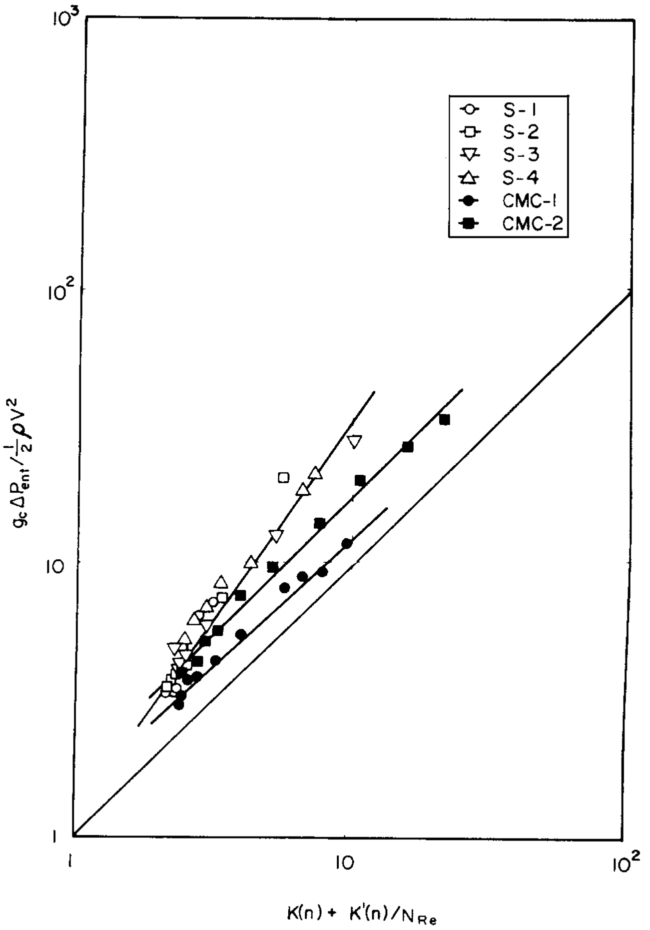

Fig. 6. Total dimensionless entrance loss vs. purely viscous contribution for viscoelastic solutions.

While it has been shown that a fluid's elastic properties can contribute a major portion of its total excess entrance pressure loss, a means of estimating and predicting this contribution would be extremely valuable for design purposes. This can be done in a rather straightforward fashion if it is assumed that the materials follow Hooke's law in shear:

$$\tau = G\gamma \qquad (6)$$

If the fluid is essentially unstressed in the upstream tube, that is, for small β (the correction is simple for larger β's) and a state of equilibrium flow is reached downstream from the contraction, the differential rate of elastic energy addition to an element of fluid passing along a streamline is

$$dE = \frac{1}{2}(\tau\gamma)\, dQ \qquad (7)$$

where all terms are functions of the radial position of the element in equilibrium flow. Combining Equations (6) and (7) we get

$$dE = \frac{(\tau(r))^2}{2G}\, dQ(r) \qquad (8)$$

Since $dQ(r) = 2\pi r v(r) dr$, $\tau(r) = \tau_w(r/R)$, and the velocity profile of a power law fluid is

$$v(r) = V\left(\frac{3n+1}{n+1}\right)\left[1 - \left(\frac{r}{R}\right)^{\frac{n+1}{n}}\right] \qquad (9)$$

Equation (8) may be written

$$dE = \frac{\pi \tau_w^2 V}{G}\left(\frac{3n+1}{n+1}\right) r \left(\frac{r}{R}\right)^2 \left[1 - \left(\frac{r}{R}\right)^{\frac{n+1}{n}}\right] dr \qquad (10)$$

Integration of Equation (10) yields

$$E = \frac{Q\tau_w^2}{G} f(n) \qquad (11)$$

where

$$f(n) = \frac{1}{4}\left(\frac{3n+1}{5n+1}\right) \quad \text{and} \quad Q = \pi R^2 V$$

Equating this rate of elastic energy addition to the overall observed rate of elastic energy loss $Q\Delta P_E$, where ΔP_E is the elastic portion of the entrance pressure loss, gives

$$\Delta P_E = \frac{\tau_w^2}{G} f(n) \qquad (12)$$

Thus, the elastic contribution to the excess entrance pressure drop should be proportional to τ_w^2. Figure 7 shows ΔP_E vs. τ_w^2 for several of the solutions and indicates strongly the validity of Equation (12) at lower shear stresses, that is, for shear rates less than about 1,000 sec.$^{-1}$. At higher shear stresses, the data show a higher-order dependence on shear stress, as might be expected from a breakdown of Hooke's law at high stresses. In view

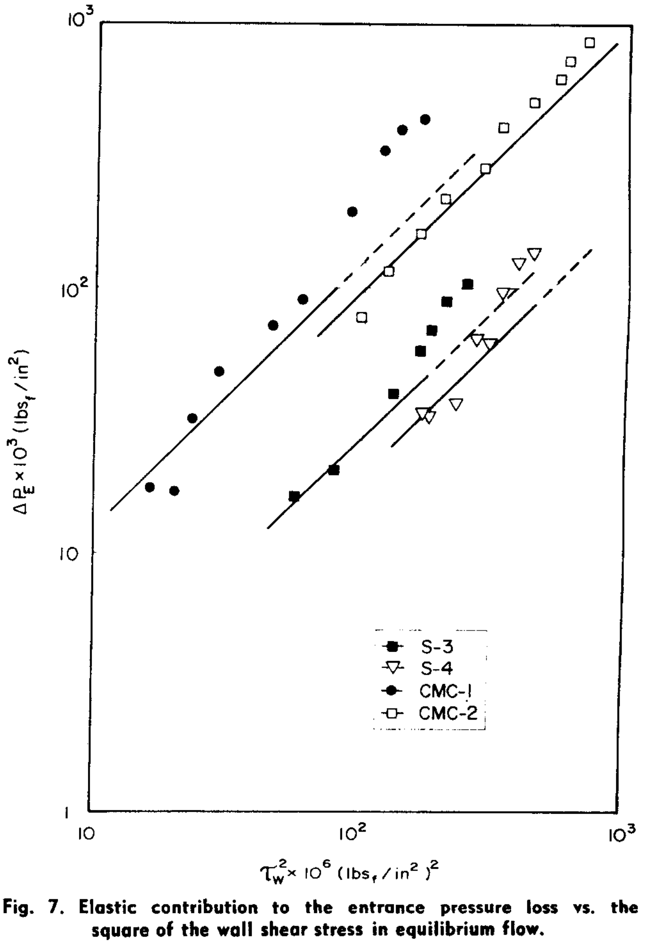

Fig. 7. Elastic contribution to the entrance pressure loss vs. the square of the wall shear stress in equilibrium flow.

of the assumptions, approximations, and the subtraction of two numbers of comparable magnitude necessary to obtain ΔP_E, the scatter is not excessive.

Values of the Hookean modulus calculated from Equation (12), and the low-stress data are given in Table 2. They show the expected increase with concentration and are of reasonable magnitude (*20*).

TABLE 2

Fluid	Conc., wt. %	$G \times 10^4$, lb.$_f$/in.^{2}
S-1	0.68	0.16
S-2	1.10	0.30
S-3	1.65	0.68
S-4	2.20	0.95

The results of the preceding development are somewhat reminiscent of work by Bagley (*3*) and Philippoff and Gaskins (*21*), but where they used an average rate of elastic energy additions characterized only by stress at the tube wall, this analysis accounts for the variations in stress and material throughput with radius. Thus, independent values of G, obtained, for example, from recoil or flow birefringence measurements (*20*), together with the usual equilibrium viscometric data, can be used to predict the elastic contribution to the entrance loss.

It is also interesting to note that while the effective entrance lengths for the viscoelastic fluids are in general greater than those for inelastic fluids, the distance required to reach equilibrium flow x_f (obtainable only approximately from the pressure profiles), though smaller than x_{eff}, showed little variation with the nature of the fluid. Typically

	Glycerol	Separan S-1
N_{Re}	2,000	3,000
x_{eff}, in.	40	77
x_f (approx.) in.	30	30

CONCLUDING REMARKS

It has been shown that viscoelastic fluids are indistinguishable from the purely viscous in steady, fully developed laminar tube flow. In the entrance region, however, their behaviors are markedly different. The effects of decreasing n and increasing elasticity with increasing solution concentration tend to compensate, the former reducing entrance losses and the latter raising them. However, elasticity accounted for up to 80% of the total entrance loss, and despite a tube L/D of 192, errors of up to 80% in the calculated friction factor were obtained if the entrance losses were not taken into account.

The procedure described for separating the purely viscous and the elastic contributions to ΔP_{ent} is the first explicit method of doing so, and although obviously in need of further experimental refinement, it contains the essential features necessary for future theoretical and experimental work. The analysis giving ΔP_E in terms of a Hookean shear modulus should be, at worst, a useful design tool, but full proof of its theoretical validity requires independent measurements of G, and its range of applicability further experimental corroboration.

ACKNOWLEDGMENT

The authors sincerely thank the National Science Foundation for support of this work.

NOTATION

D = tube diameter, in.
D_0 = reservoir diameter, in.
E = rate of elastic energy addition, in.-lb.$_f$/sec.
f = friction factor, dimensionless
G = Hookean shear modulus, lb.$_f$/in.^{2}
g_c = conversion factor, in.-lb.$_m$/lb.$_f$ sec.^{2}
K = Hagenbach coefficient, dimensionless
K' = Couette coefficient
K_p = fluid consistency index, lb.$_m$/in. sec.$^{2-n}$
L = tube length, in.
n = flow behavior index, dimensionless
N_{Re} = Reynolds number
P = pressure, lb.$_f$/sq.in.
ΔP_{ent} = excess entrance pressure drop, lb.$_f$/in.^{2}
ΔP_E = elastic entrance pressure drop, lb.$_f$/in.^{2}
Q = volumetric flow rate, in.^{3}/sec.
R = tube radius, in.
r = radial position, in.
v = axial velocity, in./sec.
V = volumetric average velocity, in./sec.
x = axial position, in.
x_f = hydrodynamic entrance length, in.
x_{eff} = effective entrance length, in.

Greek Letters

$\beta = D^2/D_0^2$ = area contraction ratio
γ = shear strain, dimensionless
$\dot{\gamma}$ = shear rate, sec.$^{-1}$
ρ = fluid density, lb.$_m$/in.^{3}
τ = shear stress, lb.$_f$/in.^{2}
τ_w = wall shear stress, lb.$_f$/in.^{2}

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Manuscript received November 25, 1968; revision received February 26, 1969; paper accepted April 2, 1969.

The Effect on Conversion of Flow Rate Variations in a Heterogeneous Catalytic Reactor

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The unsteady state behavior of a tubular heterogeneous catalytic reactor, in which significant adsorption effects occur, has been investigated theoretically and experimentally. Transient responses of conversion to step increases and decreases of flow rate as well as to periodic variations in flow rate are considered. A simplified procedure for anticipating gross effects in cyclic processes is suggested.

A mathematical model has been developed by Lehr, Yurchak, and Kabel (*1*) to predict the product distribution of a heterogeneous catalytic tubular reactor as a function of time following a step increase in flow rate. The model comprises component material balances which take the form of simultaneous partial differential equations. The rate of reaction on the catalyst surface is accounted for by extending typical Langmuir-Hinshelwood kinetics to the unsteady state. The Langmuir (monolayer) theory of activated adsorption is used to describe the adsorption rate processes and equilibria. Mass transfer effects are known to be negligible at steady state conditions (*6*) and are taken to be so in the unsteady state also (*1*). To evaluate the model, Lehr (*2*) and Kabel (*3*) performed experiments on the vapor-phase dehydration of ethanol to diethyl ether as catalyzed by ion exchange resin in the acid form:

$$2\,C_2H_5OH = (C_2H_5)_2O + H_2O \tag{1}$$

The model was found to be in qualitative agreement with all experimental observations and in quantitative agreement with many of them. The objects of the research reported in this paper are to add rigor to the model used by Lehr et al., to consider theoretically and experimentally the response of the reactor to a step decrease in flow rate, and to examine the effect of periodic variations in flow rate on production rate (or conversion) of the reactor.

The development and rationale of the model are given in complete detail elsewhere (*1, 2, 4*). Some modifications to the model of Lehr et al. have been made. In the original paper (*1*), it was assumed that the superficial velocity through the reactor could be taken as constant during the transient period. The model used in this work eliminates this assumption. The present model also achieves greater flexibility by employing a numerical integration technique along the time characteristic as well as the velocity characteristic. Other very minor changes are described, and the effects of all modifications are considered in detail by Denis (*4*). The above modifications provide the model with additional rigor which is necessary for the accurate description of the transient behaviors in this paper. However the modifications lead to no significant changes in the results of Lehr, Yurchak, and Kabel.