Measurement of Rheological Properties of Viscoelastic Fluids in Laminar Shearing Flow in Tubes

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A number of hydrodynamic flows exist which may be represented by

$$V(x_1, x_2, x_3) = V_1(x_2)\mathbf{e}_1 \qquad (1)$$

where the e_1 are orthonormal vectors. Such flows are called *laminar shearing* or *viscosimetric* and include Poiseuille flow in tubes and between parallel plates and Couette flow between parallel plates and coaxial cylinders. If one assumes that the rheological behavior of a fluid is determined by an isotropic hereditary functional of the deformation, it may be shown that the stress tensor in the velocity field specified by Equation (1) is (*4, 7*)

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{12} & \tau_{22} & \tau_{23} \\ \tau_{13} & \tau_{23} & \tau_{33} \end{vmatrix} = - \begin{vmatrix} p & o & o \\ o & p & o \\ o & o & p \end{vmatrix} + \begin{vmatrix} P_{11} & \tau_{12} & o \\ \tau_{12} & P_{22} & o \\ o & o & P_{33} \end{vmatrix} \qquad (2a)$$

where

$$p = -\frac{1}{3}\, tr\ \tau \qquad (2b)$$

It follows that the properties of such isotropic viscoelastic fluids in laminar shearing flow may be completely specified by evaluating the relationships between τ_{12} and two independent combinations of P_{11}, P_{22}, and P_{33} with shear rate. There is an extensive literature discussing experimental methods of determining the τ_{12}-shear rate relationship (for example, *10, 16*) and a growing literature of techniques to evaluate normal stresses (for example, *6, 9, 21*).

Flow in a tube may be specified by denoting the axial direction 1, the radial 2, and the angular 3. The equations of motion are

$$o = -\frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}(r\,\tau_{12}) \qquad (3a)$$

$$o = -\frac{\partial p}{\partial r} + \frac{\partial P_{22}}{\partial r} + \frac{P_{22} - P_{33}}{r} \qquad (3b)$$

$$o = -\frac{\partial p}{\partial \theta} \qquad (3c)$$

Equations (2) and (3) may be combined to give for the stress components

$$\tau_{12}(r, z) = \frac{r}{R}\,\tau_w \qquad (4a)$$

$$\tau_{11}(r, z) = -p(o, z) + P_{11} - P_{22} - \int_o^r (P_{22} - P_{33})\, d\ln r \qquad (4b)$$

$$\tau_{22}(r, z) = -p(o, z) - \int_o^r (P_{22} - P_{33})\, d\ln r \qquad (4c)$$

$$\tau_{33}(r, z) = -p(o, z) - P_{22} - \int_o^r (P_{22} - P_{33})\, d\ln r \qquad (4d)$$

A recent paper by Sakiadis (*20*) has considered the measurement of normal and shear stresses using a capillary instrument. The shear stress-shear rate relationship may be evaluated from such an experiment by the method of Weissenberg and his co-workers. Techniques for obtaining normal stresses from a capillary instrument were first investigated by Philippoff and Gaskins (*5, 6, 18*), and more recently modifications of their experiments have been published (*10, 11, 12, 1*). The Weissenberg technique, described by Sakiadis, consists of use of the relationships

$$\left(-\frac{du}{dr}\right)_w = \frac{3n' + 1}{4n'}\,\frac{8V}{D}, \qquad \tau_w = \frac{D\,\Delta p}{4L} \qquad (5a, b)$$

where

$$n' = \frac{d\ln \tau_w}{d\ln 8V/D} \qquad (5c)$$

Two experiments allowing one to evaluate $(P_{11} - P_{33})$ and $(P_{22} - P_{33})$ are discussed by Sakiadis. One experiment takes note that the reading on a pressure gauge at the exit of the tube is from Equation (4*c*)

$$P_L = -\tau_{22}(R, L) = p(o, L) + \int_o^R (P_{22} - P_{33})\, d\ln r \qquad (6)$$

Using Equation (4*a*) and differentiating Equation (6) with respect to ln τ_w yields

$$\frac{dP_L}{d\ln\tau_w} = (P_{22} - P_{33})_R + \frac{dp(o, L)}{d\ln\tau_w} \qquad (7)$$

A number of questions arise in Sakiadis's use of Equation (7) to interpret his experimental data and the results he obtains. First it is noted that straight lines are drawn through only two points in the pressure gradient profile in all except one case (see reference *20*, Figure 2) to justify fully developed flow. Only one capillary tube with L/D of 48 was used and data exists (*12, 2*) suggesting that the L/D necessary for fully developed flow for viscoelastic systems is well over 100 even at moderate Reynolds numbers. No acceptable treatment of the entrance-length problem for viscoelastic fluid systems has been published to this date. Thus it is questionable whether the data obtained in this experiment may be properly analyzed using Equation (7). Further it may be noted that Sakiadis's calculation of $(P_{22} - P_{33})_R$ gives values far in excess of τ_w which is in disagreement with the work of most experimenters (*19, 8, 3, 17, 9*) who have concluded that $(P_{22} - P_{33})_R$ is far smaller than τ_w for similar polymer-solvent systems. Two other points in this experiment may be mentioned. These are that an unknown but possibly significant experimental error (not discussed in reference *20*) exists in a technique based upon extrapolating a two point slope followed by differentiation and that the last term in Equation (7) is not investigated.

The second experiment suggested in (*20*) determines $(P_{11} - P_{33})_R$ from a capillary jet experiment. This type of experiment was first used by Gaskins and Philippoff (*5*) and has since been further developed (*10* to *15*). So that the axial normal stress can be determined accurately the expansion of a jet, it is necessary for the apparatus to be horizontal so that gravitational effects on the jet may be neglected. Making an overall momentum balance one obtains

$$\int_o^{D/2} 2\pi r \tau_{11}\, dr = \int_o^{D/2} 2\pi r \rho u^2\, dr - \frac{\pi d_j^2}{4}\rho V_j^2 \qquad (8)$$

Equation (8) may be combined with the continuity equation and differentiated with respect to τ_w to obtain (see reference *12*)

$$(\tau_{11})_R = \frac{\rho V^2}{n'}\Bigg[(n' + 1)\int_o^1 2 \left(\frac{u}{V}\right)^2 \frac{r}{R}\, d\frac{r}{R} + (2n' + 1) \left(\frac{3n' + 1}{2n' + 1} - \int_o^1 2\,\frac{r}{R}\right.$$

(*Continued from page 558*)

ABSTRACTS AND KEY WORDS

Key Words: Probability Distribution-1, Economic Variables-1, Sales Demand-6, Investment-6, Cost of Manufacture-6, Price-6, Profitability-2, Risk-2, Return on Investment-7, Monte Carlo Method-4, Sampling-4, Cost Estimating-8, Sensitivity Analysis-8, Subjective Probability-8, Bayesian Statistics-8.

Abstract: Sensitivity analyses of investment profitability provides management with the effect of changes in input variables, but no basis for estimating the likelihood of these changes occurring. Statistical techniques are available to derive the probability distribution of, and hence the risk associated with, the return-on-investment. In simple models an analytic solution is possible. More generally, the Monte Carlo Technique, a random sampling device, may be used to approximate the distribution, given subjective probability estimates of the various economic input variables.

Reference: Hess, Sidney W., and Harry A. Quigley, Chem. Eng. Progr. Symposium Ser, No. 42, 59, p. 55 (1963).

Key Words: Evaporation-7, Vacuum-5, Compatibility-7, Aerospace-8, Stability-6, Methods-8, Volatility-6, Vaporization-7, Outgassing-7, Knudsen cell-10, Space-5, Grease-1, Testing-8, Microbalance-10, Plastics-1, Oil-1.

Abstract: Continuous weight measurement during vacuum exposure evaporation studies is recommended, especially for engineering materials in which vaporization rates vary because of the heterogeneity of the materials.

A test method giving more refined information than is now available is proposed as a standard for correlation of results between laboratories. Use of Knudsen cell concept is a further improvement.

Experimental work giving better than 1% reproducibility on pure and engineering materials is reported for vapor pressures down to 10^{-5} mm. mercury. The bulk of the studies concern plastics and eighteen oils and greases.

Reference: Birkhahn, Paul D., Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 64 (1963).

Key Words: Queueing Theory-1, Random Process-1, Statistics-1, Probability Theory-1, Inventory-2, Computer-10.

Abstract: The application of the mathematical theory of queues to problems of inventory control–introductory and general, primarily the definition of fundamental concepts–is outlined.

Reference: Petersen, D. R., Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 71 (1963).

Key Words: Queuing Theory-1, Random Arrival Rate-1, Poisson Arrival Rate-1, Batches-1, Reactors-10, Queue-3, Waiting Line-3, Lost Time-3, Stills-10, Distillation Columns-10, Random Service Rate-2, Negative Exponential Service-2, Computer-10, Design-9, Optimization-9, Costs-8.

Abstract: A battery of reactors discharges batches in a random (Poisson) pattern to another bank of reactors (stills) for further processing for various time periods (negative exponential). Lost time was encountered in the first bank of reactors because sometimes all the stills in the second bank were occupied and in effect resulted in a queue or waiting line of batches in the first bank waiting for service by the second bank. Queuing theory equations permit computation of expected lost time because batches have to wait in the primary reactors thus preventing recharging. Optimum equipment balance needed to minimize cost can be calculated, preferably with a computer because of the complexity of the mathematical equations.

Reference: Stover, Albert M., Chem. Eng. Progr. Symposium Ser. No. 42, 59, p. 74 (1963).

(*Continued on page 562*)

$$\left(\frac{u}{V}\right)^2 d\frac{r}{R}\Big) - \left(\frac{D}{d_j}\right)^2 \left(n' + 1 + \frac{d\ln(D/d_j)}{d\ln(8V/D)}\right)\Big] \tag{9a}$$

$$= -p(o, L) + (P_{11} - P_{22})_R - \int_o^R (P_{22} - P_{33})\, d\ln r \tag{9b}$$

and from Equation (6)

$$(\tau_{11})_R = -P_L + (P_{11} - P_{33})_R - (P_{22} - P_{33})_R \tag{9c}$$

Equations (9) to (10) are equivalent to, but somewhat more susceptible to experimental evaluation than, the expressions derived in reference *20*.

Sakiadis claims that $(\tau_{11})_R$ is negligible and obtains $(P_{11} - P_{33})_R$ from Equation (10) by considering both $(\tau_{11})_R$ and $p(o, L)$ to be zero. The main reason for concluding $(\tau_{11})_R$ to be negligible appears to be that he notes that the experimental value of P_L is

$$P_L > 25\,\rho V^2 \int_o^1 2\left(\frac{u}{V}\right)^2 \frac{r}{R}\, d\frac{r}{R}$$

and as

$$[(\tau_{11})_R]_{\max} = \left(\frac{n'+1}{n'}\right) \rho V^2 \int_o^1 2\left(\frac{u}{V}\right)^2 \frac{r}{R}\, d\frac{r}{R}$$

therefore

$$P_L > 25\,\frac{n'}{n'+1}\,[(\tau_{11})_R]_{\max}$$

The question of the significance of the measurement of P_L has already been noted and the implausible results that this measurement gives for $(P_{22} - P_{33})_R$ have been pointed out. Thus the reported values of $(P_{11} - P_{33})_R$ are open to serious question.

In regard to the experimental technique discussed in reference *20* to obtain d_j/D, it is noted that the maximum diameter of a vertical jet is suggested for use in calculation for the diameter where the axial normal stress has completely relaxed. To assume that the normal stresses have relaxed at this point is completely unfounded. Also as has been pointed out in reference *12* and verified by Bagley (*2*), d_j/D varies strongly with L/D until L/D is greater than 100 even at moderate Reynolds numbers, while Sakiadis has used one tube with L/D of 48. Further, the work in reference *20* takes no cognizance of the Middleman-Gavis effect (*14, 15, 13*) which is often quite significant in experiments of this nature.

In conclusion it is noted that in reference *20* there is a discussion of two interesting experimental methods for the calculation of normal stresses in laminar shearing flows of viscoelastic fluids. Unfortunately, it appears that the methods have not been used as carefully as necessary thus causing aberrations in the results.

NOTATION

D = tube diameter
d_j = jet diameter
L = length of tube
n' = $d(\ln \tau_w)/d(\ln 8v/D)$
P_{ij} = components of deviatoric stress tensor
p = isotropic stress pressure
R = tube radius
r = radius
u = point velocity
V = average velocity
V_j = jet velocity
x_i = orthogonal direction
z = axial direction
τ_{ji} = component of stress tensor
τ_w = wall shear stress

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The Influence of Operating and Static Liquid Holdups on Gas Absorption Rates in Chemically Reacting Systems

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An apparent anomaly which has been encountered repeatedly in packed tower studies of gas absorption with a rapid, irreversible chemical reaction is the observation of overall mass transfer coefficients which are far greater than the corresponding gas-phase mass transfer coefficients calculated from physical absorption data. Typically, the overall coefficient increases with increasing liquid-phase reactant concentration, eventually exceeding the physical absorption value of the gas-phase coefficient, frequently by a very considerable extent. Several investigators have shown that the overall coefficient becomes constant when the liquid-phase reactant concentration is increased sufficiently.

An explanation of these results was proposed by Shulman, Ullrich, and Wells (*7*) who visualized the interfacial area of the liquid in a packed tower to consist of the surfaces of both rapidly moving streams and quiescent accumulations. In the case of physical absorption, the effective interfacial area is that of the rapidly flowing liquid. In the case of absorption with a rapid, irreversible chemical reaction, the presence of the liquid-phase reactant raises the absorptive capacity of the quiescent liquid. This liquid, even with its low rate of replacement, eventually becomes as effective as the rapidly moving streams at high concentrations of the liquid-phase reactant. Then the total interfacial area is effective for mass transfer. The principal experimental verification of this hypothesis is the following relation which has been demonstrated for packed tower operation (*6*):

$$\frac{(k_G a)_{r,v}}{(k_G a)} = C \frac{h_t}{h_o} \qquad C \sim 1.0 \qquad (1)$$

The sum of the static holdup, h_s, composed of the quiescent accumulations of liquid, and the operating holdup, h_o, composed of the rapidly flowing liquid, is equal to the total holdup of liquid in the packing, h_t. All the holdups are expressed in units of liquid volume per unit packed volume. It has also been pointed out that for vaporization of liquids in packed towers, the entire liquid surface area should be effective for mass transfer (*7*). If the model is to be consistent, it must predict an eventual decrease in the gas-phase mass transfer coefficient when there is an increase in the rate at which the quiescent liquid approaches saturation, regardless of how this increase is accomplished. On this basis, Shulman, Ullrich and Wells (*7*) predicted for cases of absorption with a rapid, irreversible chemical reaction a decrease in the gas-phase mass transfer coefficient as the gas-phase solute concentration is increased. In descriptive terms, as the gas-phase solute concentration is decreased, the quiescent accumulations of liquid in the packing become increasingly effective for absorption since they require a longer time to become saturated. Also, an increase in the effective interfacial

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