l, L = length defined in Figure 1
x, y = coordinates
r = effective reaction rate, Equation (4)
r_n = reaction rate on patch n in Equation (1)
$\overline{r}_{\max}$ = average effective reaction rate, Equation (1)
S = selectivity, Equation (8)

Greek Letters

δ = boundary layer thickness
η = effectiveness factor, Equations (5) and (6)

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Manuscript received January 17, 1975; revision received March 27 and accepted March 31, 1975.

Mechanics of Steady Spinning of a Viscoelastic Liquid

MORTON M. DENN
CHRISTOPHER J. S. PETRIE
Department of Chemical Engineering
University of Delaware
Newark, Delaware

and
PIERRE AVENAS
Centre de Mise en Forme des Materiaux
Ecole Nationale Superieure des Mines de Paris
Paris, France

The equations for steady isothermal spinning of a viscoelastic liquid are solved for a fluid model with constant modulus and a single constant relaxation time. High stress levels are predicted for elastic liquids, and the velocity approaches a linear profile in the limit of maximum drawdown. These predictions are in accordance with the observed behavior of polymeric liquids in isothermal spinning. Relaxation times computed from spinning data of Spearot and Metzner and Acierno et al. for four low density polyethylene melts are comparable to those measured rheogoniometrically, though the spinning relaxation times are 20 to 80% larger.

SCOPE

Spinning is the process of drawing a liquid into a filament or a sheet. The mechanics of steady spinning of low molecular weight Newtonian liquids is well understood, with good agreement between theory and experiment. The steady spinning of viscoelastic polymer melts and solutions, in contrast, is not well understood. There are major qualitative differences in the velocity and diameter profiles observed in the spinning of Newtonian and polymeric liquids. No analysis which can explain these differences has been published. Very high stresses are observed experimentally in the spinning of polymeric liquids relative to the stresses in a Newtonian liquid of the same viscosity under comparable processing conditions. These stresses cannot be predicted quantitatively, and the qualitative theoretical expectation of high stresses is usually founded on an a priori assumption of the kinematics in combination with an analogy to uniform transient stretching.

The industrial importance of spinning is only one reason for interest in the process. Spinning is an extensional flow field and it is usually a high Deborah number process; that is, large stress changes occur over a time scale which is comparable to the fluid relaxation time. In this sense, it is a prototype of many practical polymer processing situations, which tend to be high Deborah number processes with an important extensional component in the flow field. In contrast, nearly all analyses of the flow of polymeric liquids which have been successfully compared with experiments have been for shearing flows with no extensional component or for low Deborah number perturbations about Newtonian behavior. The extent to which in-

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C. J. S. Petrie is with the Department of Engineering Mathematics, University of Newcastle upon Tyne, Newcastle upon Tyne, England.

formation about fluid behavior which is obtained in the latter classes of experiments can be applied to practical processing situations remains an open question.

This paper reports on a solution of the problem of steady isothermal spinning for a viscoelastic liquid and a comparison with available experiment. The constitutive equation for the stress is a slight generalization of the Maxwell material. This is restrictive in that material parameters are assumed to be constant and the fluid is characterized by a single relaxation time. The equation does describe the important qualitative features of viscoelastic materials in shear flow, however, and it can be applied to high Deborah number situations.

CONCLUSIONS AND SIGNIFICANCE

The solution to the spinning problem exhibits the features observed in laboratory experiments of isothermal spinning. There is a smooth transition from Newtonian to viscoelastic behavior. High stresses are predicted for sufficiently large values of a dimensionless viscoelastic parameter, and a velocity profile which is nearly linear in distance along the filament is obtained in the region of high stress. The high stress flow conditions correspond to a high Deborah number process, with a processing time corresponding to approximately one relaxation time.

In the high stress region the tensile force is too sensitive to small variations in the fluid relaxation time to allow meaningful direct comparison with experiment by using the shear relaxation time to predict the force. On the other hand, relaxation times can be estimated from the measured forces. For four low density polyethylene melts, the relaxation times computed using the spinning theory are comparable to those measured in shear, although the former tend to be 20 to 80% higher. Considering the approximate nature of the constitutive equation, this is a good agreement but it is not close enough to completely resolve the question of the direct applicability of shear measurements to extensional flow.

Polymer melts and solutions show stress levels in spinning which are one or more orders of magnitude larger than the stresses that would be observed in a low molecular weight liquid of comparable viscosity. In addition, the diameter profile along the molten threadline is qualitatively different in polymeric and Newtonian liquids. The large stresses have been explained qualitatively by a priori assumptions about the kinematics and analogy with the transient uniform stretching of an elastic liquid (for example, Chen et al., 1972; Spearot and Metzner, 1972). The analogy is misleading with respect to the stress behavior in steady spinning, however, and the approach cannot account for the kinematical differences observed in polymeric liquids.

The mechanics of steady spinning of Newtonian liquids has been studied by Matovich and Pearson (1969), together with extensions to shear-dependent inelastic liquids and the second-order fluid approximation to viscoelastic behavior. The Matovich and Pearson analysis accurately describes the stresses and kinematics in the spinning of viscous Newtonian liquids (for example, Mewis and Metzner, 1974; Weinberger and Goddard, 1974). The second-order fluid solution is not adequate to describe even the proper qualitative behavior observed for polymeric liquids, however. This is because steady spinning is usually a high Deborah number process (Metzner et al., 1966) in which large stress changes occur over a Lagrangian time scale which is of the same order as the characteristic relaxation time of the fluid. The second-order fluid is not a valid approximation to the stress behavior of real viscoelastic liquids under such conditions.

An approximate solution of the mechanics of steady spinning of a Maxwell material was obtained by Zeichner (1973) as part of a study of spin-line stability. His results are summarized in Denn (1975). The Maxwell material exhibits stress relaxation and is a valid stress constitutive equation at high Deborah number. Zeichner's solution predicts high tensile stresses under certain processing conditions and an approach to a kinematical region in which the velocity varies linearly along the threadline. These are the kinematics observed in laboratory studies on the isothermal spinning of polyethylene melts (Spearot and Metzner, 1972) and aqueous polymer solutions (Kanel, 1972). The solution is based on an a priori assumption regarding the relative magnitudes of various normal stress terms, and the validity of this assumption cannot be established within the framework of the analysis. The ordering argument is known to be invalid in the limit of Newtonian fluid behavior.

We report here a solution to the problem of steady isothermal spinning without any a priori assumptions about the normal stresses. The solution illustrates the manner in which the imposed force and fluid rheological properties interact in passing from the low stress, Newtonian fluid flow field to the high stress, linear kinematics characteristic of polymeric liquids. An approximate analytical solution in the limit of high stresses compares favorably with available spinning data.

CONSTITUTIVE EQUATION

In order to describe the mechanics of a high Deborah number process such as spinning, it is necessary to model the fluid stress state by a constitutive equation which allows for stress relaxation. The simplest such representation is the Maxwell material. We use here a slight generalization of the classical Maxwell material, employed by Sun and Denn (1972), which has the form

$$\boldsymbol{\tau} + \lambda \frac{\mathfrak{d}\boldsymbol{\tau}}{\mathfrak{d}t} = \mu \mathbf{A} + 2\lambda\mu\nu \mathbf{A}^2 \tag{1}$$

$$\mathbf{A} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T \tag{2}$$

$\boldsymbol{\tau}$ is the extra-stress and $\mathbf{v}$ the velocity. $\mathfrak{d}/\mathfrak{d}t$ is Oldroyd's convected derivative for contravariant tensors, which can be written for cartesian coordinates as

$$\frac{\mathfrak{d}\tau^{ij}}{\mathfrak{d}t} = \frac{\partial \tau^{ij}}{\partial t} + \sum_k v^k \frac{\partial \tau^{ij}}{\partial x^k} - \sum_k \frac{\partial v^i}{\partial x^k} \tau^{kj} - \sum_k \frac{\partial v^j}{\partial x^k} \tau^{ik} \tag{3}$$

There are three material parameters λ, μ, and ν. The Maxwell material is recovered by setting $\nu = 0$. The second-order fluid is obtained by expanding Equation (1) in the dimensionless product $\lambda||\mathbf{A}||$, where $||\mathbf{A}||$ is the norm of $\mathbf{A}$ and λ is the characteristic relaxation time,

$$\lambda \|\mathbf{A}\| \to 0: \quad \boldsymbol{\tau} = \mu \mathbf{A} - \lambda\mu \frac{\mathfrak{d}\mathbf{A}}{\mathfrak{d}t} + 2\lambda\mu\nu\mathbf{A}^2 + o(\lambda\|\mathbf{A}\|) \tag{4}$$

The material parameters can be interpreted in terms of rheogoniometric measurements by considering a simple shearing flow,

$$v^1 = v^1(x^2), \quad v^2 = v^3 = 0 \tag{5}$$

The stress field is readily established to be

$$N_1 \equiv \tau^{11} - \tau^{22} = 2\lambda\mu\gamma_s^2 \, (1 + 2\nu\lambda^2\gamma_s^2) \tag{6a}$$

$$N_2 \equiv \tau^{22} - \tau^{33} = 2\nu\lambda\mu\gamma_s^2 \tag{6b}$$

$$\tau^{12} = \mu\gamma_s \, (1 + 2\nu\lambda^2\gamma_s^2) \tag{6c}$$

$$\gamma_s \equiv \frac{dv^1}{dx^2} \tag{6d}$$

Then

$$\mu = \lim_{\gamma_s \to 0} \frac{\tau^{12}}{\gamma_s} \tag{7a}$$

$$\nu = \lim_{\gamma_s \to 0} \frac{N_2}{N_1} \tag{7b}$$

$$\lambda = \frac{N_1}{2\gamma_s\tau^{12}} \tag{7c}$$

Thus μ can be interpreted as a zero-shear viscosity and ν as the zero-shear limit of the ratio of secondary to primary normal stress difference. The Maxwell material, with $\nu = 0$, does not admit a nonzero secondary normal stress difference. ν appears to be negative and small for most systems studied, in which case Equations (6a) and (6c) predict slight shear thinning of the viscosity and primary normal stress coefficient. The viscosity curves for the molten polyethylenes studied by Spearot (1972) suggest a value of approximately $\nu \approx -0.1$. Equation (7c) is the conventional equation for estimating the fluid relaxation time from steady rheogoniometric measurements.

Any generalization of the Maxwell model which attempts to introduce a degree of shear thinning by the inclusion of quadratic terms has a limiting shear rate beyond which the shear stress curve becomes double valued and stable shear flow could not be maintained. For Equation (1) this limit is

$$\lambda^2\gamma_s^2 < \frac{1}{-6\nu} \tag{7d}$$

For $\nu = -0.1$ this limit becomes $\lambda\gamma_s < 1.3$, which includes the range of the data to be considered subsequently.

SPINNING EQUATIONS

The spinning of a round filament is shown schematically in Figure 1. The liquid column swells in the region immediately downstream of the point of extrusion. This region of die swell is not treated in the analysis, and the origin of the coordinate system is taken at a position beyond the point of maximum diameter where the axial velocity has become approximately uniform over the cross section. The fiber is wound up at $z = L$ at a velocity greater than the extrusion velocity, resulting in a steadily decreasing diameter from $z = 0$ to $z = L$. We analyze only isothermal experiments in which the filament remains a liquid for its entire length. This is a simpler situation than in commercial spinning, where crystallization will occur.

Fig. 1. Schematic of the drawing of a filament.

The assumptions in writing the momentum equation are outlined by Matovich and Pearson (1969). The filament curvature is assumed to be small, and only first-order terms in curvature are retained. In addition, the axial velocity v^z is taken to depend only on axial position z. This latter assumption has been shown experimentally to be a good one (Kanel, 1972; Baid, 1973). We further assume here that only viscous and viscoelastic forces are important and that effects of inertia, gravity, and surface tension may be neglected. Denoting v^z by v, the momentum balance may then be written

$$\tau^{zz} - \tau^{xx} = \frac{Fv}{Q} \tag{8}$$

τ^{xx} is numerically equal to the isotropic pressure in this approximation. F is the imposed force to draw the filament, and it is constant along the threadline. Q is the volumetric flow rate of extruded liquid, which is also constant.

With the further assumption that certain shearing terms are small and the use of the continuity equation the z- and x-components of the constitutive equation are

$$\tau^{zz} + \lambda \left[v \frac{d\tau^{zz}}{dz} - 2\tau^{zz} \frac{dv}{dz} \right] = 2\mu \frac{dv}{dz} + 8\lambda\mu\nu \left(\frac{dv}{dz} \right)^2 \tag{9}$$

$$\tau^{xx} + \lambda \left[v \frac{d\tau^{xx}}{dz} + \tau^{xx} \frac{dv}{dz} \right] = -\mu \frac{dv}{dz} + 2\lambda\mu\nu \left(\frac{dv}{dz} \right)^2 \tag{10}$$

The neglected shearing terms can be shown to be of the order of $(R/L)^2$, where R is the filament radius.

The proper boundary conditions for the solution of Equations (8), (9), and (10) are not completely evident since the initial diameter at $z = 0$ is unknown. For analytical purposes we shall take the initial velocity as given, and the windup velocity may always be specified. Thus, the boundary conditions for the velocity are

$$v(0) = v_0, \quad v(L) = D_R v_0 \tag{11a,b}$$

D_R is the draw ratio based on maximum diameter. In addition, we shall need an initial condition on τ^{zz}. Mathematically, this is necessary because the order of the differential equations is one greater than for a Newtonian liquid. Physically, the necessity for this condition is best understood in terms of the elastic memory of a Maxwell liquid. Unlike a Newtonian liquid, the stress state of the viscoelastic liquid depends on its prior processing, and we must specify what the fluid remembers of the flow upstream of the region we are considering (compare Petrie, 1973). Specification of one extra stress uniquely determines the other through the momentum equation (8), so we require the single additional boundary condition

$$\tau^{zz}(0) = \tau_0 \tag{11c}$$

We shall discuss the role played by this stress boundary condition further below.

It is useful to define dimensionless variables as follows:

$$u = v/v_0 \quad \xi = z/L$$

$$T = \tau^{zz}\, Q/Fv_0 \quad P = \tau^{xx}\, Q/Fv_0$$

Equations (8) through (11) then become

$$T - P = u \tag{12}$$

$$T + \alpha\left[u\frac{dT}{d\xi} - 2T\frac{du}{d\xi}\right] = 2\epsilon\frac{du}{d\xi} + 8\alpha\epsilon\nu\left(\frac{du}{d\xi}\right)^2 \tag{13}$$

$$P + \alpha\left[u\frac{dP}{d\xi} + P\frac{du}{d\xi}\right] = -\epsilon\frac{du}{d\xi} + 2\alpha\epsilon\nu\left(\frac{du}{d\xi}\right)^2 \tag{14}$$

$$u(0) = 1, \quad u(1) = D_R, \quad T(0) = T_0 \tag{15}$$

where $T_0 = \tau_0\, Q/Fv_0$. The dimensionless groups α and ϵ are defined

$$\alpha = \frac{\lambda v_0}{L}, \quad \epsilon = \frac{\mu Q}{FL}$$

Thus, ϵ is a reciprocal dimensionless force, while α is the primary viscoelastic parameter.

For interpretive purposes it should be noted that the relaxation time λ can be expressed in terms of an elastic shear modulus G

$$\lambda = \frac{\mu}{G} \tag{16}$$

The ratio ϵ/α, which arises in the analysis, can then be written

$$\frac{\epsilon}{\alpha} = \frac{G}{F/A(0)} \tag{17}$$

where $A(0)$ is the initial cross-sectional area. Thus, this ratio of parameters is the ratio of the characteristic stress of the material to the initial imposed stress.

VELOCITY EQUATION

Equations (12) through (14) can be manipulated to yield a single second-order differential equation for the velocity. First, Equation (12) is substituted in (14), and the resulting equation is subtracted from Equation (13) to yield

$$T = \frac{1}{3\alpha}\,\frac{u}{\dfrac{du}{d\xi}} + \frac{2}{3}u - \frac{\epsilon}{\alpha} - 2\epsilon\nu\frac{du}{d\xi} \tag{18}$$

Equation (18) is then substituted into Equation (13) to give

$$\frac{u}{\dfrac{du}{d\xi}} - 3\epsilon + \alpha u - \alpha\frac{u^2\dfrac{d^2u}{d\xi^2}}{\left(\dfrac{du}{d\xi}\right)^2} - 2\alpha^2 u\frac{du}{d\xi} - 6\alpha\epsilon\nu\frac{du}{d\xi}$$

$$- 12\alpha^2\epsilon\nu\left(\frac{du}{d\xi}\right)^2 - 6\alpha^2\epsilon\nu u\frac{d^2u}{d\xi^2} = 0 \tag{19}$$

Solutions of Equation (19) with $du/d\xi < 0$ initially must have $du/d\xi < 0$ for all ξ and cannot give a draw ratio which exceeds unity. If $du/d\xi > 0$ initially then it remains positive and u increases monotonically. Specification of the initial value of $du/d\xi$ is equivalent, through Equation (18), to specification of T_0. The requirement that the initial velocity derivative be positive and that it be real restricts the initial stress to values

$$T_0 > \frac{2}{3} - \frac{\epsilon}{\alpha} + \frac{2}{3}\sqrt{-6\nu\frac{\epsilon}{\alpha}} \tag{20}$$

Solutions are further restricted to values of ν satisfying the inequality

$$-6\alpha\epsilon\nu(du/d\xi)^2 < u \tag{21}$$

This inequality will certainly not be violated for $-0.15 \leq \nu \leq 0$ for a solution whose initial conditions satisfy (21).

Equation (19) can be solved numerically by any standard initial value technique if we know u and $du/d\xi$ at $\xi = 0$. The latter is obtained from Equation (18) in terms of T_0, which is known in principle. The solution gives the value $u(1)$ in terms of α, ϵ, ν, and T_0, and by varying ϵ this value is adjusted until it satisfies the condition $u(1) = D_R$, Equation (15). This iterative calculation corresponds to the physical idea of varying the applied force until the desired draw ratio is obtained. The stresses T and P are obtained from Equations (18) and (12) once the velocity is known.

Before numerical calculations are presented it is useful to examine some asymptotic cases for which analytical solutions can be obtained. These limiting solutions elucidate the behavior to be expected from the general case. One result of considerable significance is that the structure of the solution is relatively insensitive to the value of the initial stress T_0. This is quite useful since it is unlikely that T_0 will be known in any particular application.

LIMITING BEHAVIOR: $\alpha \to 0$

An approximate solution can be obtained as an asymptotic series in α for nearly Newtonian liquids, when α is small. This is the region of small Deborah number, where the liquid relaxation time is small compared to the time for flow along the filament. The solution is a singular perturbation about Newtonian behavior since for $\alpha = 0$ the order of the differential equation is reduced and the stress boundary condition cannot be satisfied for arbitrary T_0. (This aspect of the problem, which also arises for a second-order fluid, is discussed briefly by Matovich and Pearson, 1969). The method of matched asymptotic expansions is used to solve the singular perturbation problem. In this method we obtained an inner solution, valid near $\xi = 0$, and an outer solution, valid for $\alpha \to 0$ with fixed $\xi > 0$. The solutions are required to agree on a term-by-term basis in the region of overlap, thus defining the overall solution.

The outer solution is

$$u = (U_0 + \alpha U_1 + \alpha^2 U_2)e^{\xi/3\epsilon}$$

$$- \frac{2\alpha\nu}{3\epsilon}(U_0 + 2\alpha U_0 U_1)e^{2\xi/3\epsilon}$$

$$- \frac{\alpha^2 U_0^3}{9\epsilon^2}(1 + 2\nu - 8\nu^2)e^{3\xi/3\epsilon} + o(\alpha^2) \tag{22a}$$

$$T = \frac{2}{3}(U_0 + \alpha U_1 + \alpha^2 U_2)e^{\xi/3\epsilon}$$

$$+ \frac{2\alpha}{9\epsilon}(U_0^2 + 2\alpha U_0 U_1)e^{2\xi/3\epsilon}$$

$$- \frac{2\alpha^2 U_0^3}{9\epsilon^2}(1 + 4\nu + \frac{8}{3}\nu^2)e^{3\xi/3\epsilon} + o(\alpha^2) \tag{23a}$$

This solution could be made to satisfy the boundary condition $u(0) = 1$ by a suitable choice of the constants of integration U_0, U_1, and U_2, but then T_0 would necessarily take on the value $2/3 + 2\alpha(1 + 2\nu)/9\epsilon - 4\alpha^2(1 + 3\nu + 4\nu^2)/27\epsilon^2$.

The inner solution, valid near $\xi = 0$, is obtained by changing the independent variable from ξ to $x = \xi/\alpha$ and expanding in α for fixed x. Because we are considering the region near $\xi = 0$, this solution must satisfy the initial conditions $u(0) = 1$, $T(0) = T_0$. The result is

$$u = 1 + \frac{\alpha x}{3\epsilon} + \frac{\alpha^2 x^2}{18\epsilon^2} - \frac{\alpha^2}{3\epsilon^2}\left(T_0 - \frac{2}{3}\right)(1 - e^{-x}) - \frac{2\alpha^2 \nu x}{9\epsilon^2} + o(\alpha^2) \quad (22b)$$

$$T = T_0 e^{-x} + \frac{2}{3}(1 - e^{-x}) + \frac{2\alpha}{9\epsilon}(1 + x - e^{-x}) + \frac{\alpha}{6\epsilon}\left(T_0 - \frac{2}{3}\right) x^2 e^{-x} + \frac{4\alpha\nu}{9\epsilon}(1 - e^{-x}) + o(\alpha) \quad (23b)$$

We omit the α^2 term in the equation for T since it is long and does not introduce any new feature.

We obtain the composite expansion, which satisfies the conditions $u(0) = 1$, $T(0) = T_0$ and is uniformly valid as $\alpha \to 0$ for all ξ in the interval $0 < \xi < 1$, by matching the inner and outer solutions. For example, the first three terms in the inner expansion for u, Equation (22b), may be recognized as the first three terms in a series expansion of the outer term $U_0 \exp(\xi/3\epsilon)$ if $U_0 = 1$. The composite expansion is

$$u = \left[1 + \frac{2\alpha\nu}{3\epsilon} + \frac{\alpha^2}{9\epsilon^2}(3 - 3T_0 + 2\nu)\right] e^{\xi/3\epsilon} - \frac{2\alpha\nu}{3\epsilon}\left[1 + \frac{4\alpha\nu}{3\epsilon}\right] e^{2\xi/3\epsilon} - \frac{\alpha^2}{9\epsilon^2}[1 + 2\nu - 8\nu^2] e^{3\xi/3\epsilon} + \frac{\alpha^2}{9\epsilon^2}[3T_0 - 2] e^{-\xi/\alpha} + o(\alpha^2) \quad (24)$$

$$T = \frac{2}{3}\left[1 + \frac{2\alpha\nu}{3\epsilon}\right] e^{\xi/3\epsilon} + \frac{2\alpha}{9\epsilon} e^{2\xi/3\epsilon} + \left[\left(T_0 - \frac{2}{3}\right)\left(1 + \frac{\xi^2}{6\alpha\epsilon}\right) - \frac{2\alpha(1 + 2\nu)}{9\epsilon}\right] e^{-\xi/\alpha} + o(\alpha) \quad (25)$$

This shows all the features we expect physically for a small α solution. For zero α we recover the Newtonian solution $u = \exp(\xi/3\epsilon)$, $T = 2u/3$ (Matovich and Pearson, 1969), while for small α the term $\exp(-\xi/\alpha)$ decays extremely rapidly. Thus, the stress initial condition only affects the flow close to $\xi = 0$, consistent with the idea that the fluid has a short memory. It is only at order α^2 that T_0 appears in a term that does not decay, and hence if $\alpha^2 T_0/\epsilon^2$ is small compared to unity, we can ignore the influence of T_0 on the stress and velocity profiles except very close to $\xi = 0$.

Physically, it is useful to note that outside the boundary layer near $\xi = 0$ the small parameter α always appears in the ratio α/ϵ. Thus, the perturbation expansion can be interpreted as one for conditions in which the applied stress $F/A(0)$ is small compared to the characteristic fluid stress, G. The Newtonian limit is one in which the shear modulus becomes infinite and the ratio α/ϵ goes to zero.

The relationship between the draw ratio $D_R = u(1)$ and the dimensionless applied force $1/\epsilon$ used to pull the filament can be obtained from the velocity equation. The result is

$$\epsilon = \frac{1}{3 \ln D_R}[1 - 2\alpha\nu(D_R - 1) - 8\alpha^2\nu^2(D_R - 1)] + \alpha^2\left[1 - T_0 - \frac{D_R^2}{3} - \frac{2\nu}{3}(D_R - 1)^2 + \frac{\nu^2}{6}(D_R - 1)(5D_R - 1)\right] + o(\alpha^2) \quad (26)$$

This shows that the effect of the fluid elasticity parameter α is to increase the force $(1/\epsilon)$ required to obtain a given draw ratio. The effect of a negative ratio of secondary to primary normal stress coefficient is to decrease the force. The results, as far as comparison is possible, do not appear to be consistent with those of Matovich and Pearson (1969).

LIMITING SOLUTION: $\frac{\epsilon}{\alpha} \to 0$

The asymptotic behavior under conditions in which the imposed stress is large compared to the modulus, $\epsilon/\alpha \to 0$, is of practical processing interest and corresponds to the conditions under which controlled laboratory isothermal spinning experiments have been carried out (Kanel, 1972; Spearot and Metzner, 1972). The problem is not singular in this limit, and the zero-order term can be obtained exactly in the implicit form

$$u + \frac{1}{2} k \ln\left\{\frac{|u - k|^3 \, |1 - k^3|}{|u^3 - k^3| \, |1 - k|^3}\right\} - k\sqrt{3}\left\{\tan^{-1}\left(\frac{2u + k}{k\sqrt{3}}\right) - \tan^{-1}\left(\frac{2 + k}{k\sqrt{3}}\right)\right\} = 1 + \frac{\xi}{\alpha} \quad (27)$$

The constant of integration k^3 must lie in the range $-\frac{1}{2} < k^3 < 1$, where k^3 is related to the initial stress by

$$k^3 = 1 - T_0^{-1}$$

This bound is thus equivalent to Equation (20) for $\epsilon/\alpha = 0$. We may note in passing that $k^3 = P(0)/T(0)$, the ratio of extra normal stresses in the radial and axial directions at $\xi = 0$. Furthermore

$$\frac{P(\xi)}{T(\xi)} = \frac{k^3}{[u(\xi)]^3} \quad (28)$$

In this limit, as the velocity develops the ratio of radial to axial stress rapidly becomes small irrespective of the initial ratio. When $u = 3$, corresponding to threefold area reduction, the maximum value of $|P/T|$ is less than 0.04. Spearot (1972) and Zeichner (1973) previously assumed that $P/T = 0$ for spinning of a Maxwell fluid.

Equation (27) is plotted in Figure 2 for the admissible values of k^3. All velocity functions become linear, and the profiles for all but very large values of T_0 do not differ markedly from the profile for $k^3 = 0$, $T_0 = 1$, which is simply a straight line,

$$T_0 = 1: \quad u = T = 1 + \frac{\xi}{\alpha} \quad (29)$$

The family of solutions is bounded from above by the solution for $k^3 = -\frac{1}{2}$. Since the draw ratio D_R corresponds to the velocity at $\xi = 1$, this means that for fixed α there is a maximum draw ratio that can be achieved, defined by values along the bounding curve $k^3 = -\frac{1}{2}$. This limiting value is given approximately by

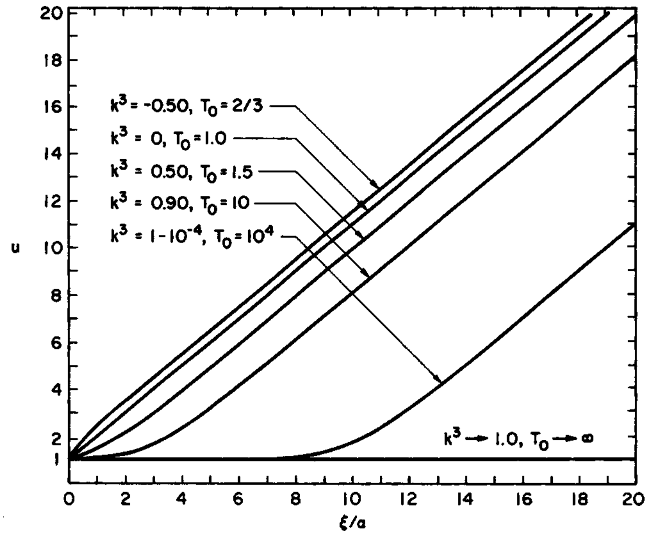

Fig. 2. Dimensionless velocity as a function of ξ/α, $\epsilon/\alpha = 0$.

$$D_R = 1.63 + \alpha^{-1} \tag{30}$$

The next term in the asymptotic series in ϵ/α can be obtained by means of a regular perturbation expansion. For simplicity we record only the result for solutions close to the linear solution $T_0 = 1$ given by Equation (29), taking as initial conditions $u(0) = 1$, $T(0) = 1 + \epsilon/\alpha\, T_1$. The result is

$$u = 1 + \frac{\xi}{\alpha} + \frac{\epsilon}{\alpha}\left\{ -\frac{3}{2}(1+6\nu)\ln\left(1+\frac{\xi}{\alpha}\right) - \frac{3}{4}(2T_1 + 1 - 2\nu)\left[1 - \frac{\alpha^2}{(\alpha+\xi)^2}\right]\right\} + o\left(\frac{\xi}{\alpha}\right) \tag{31}$$

$$T = 1 + \frac{\xi}{\alpha} + \frac{\epsilon}{\alpha}\left\{ T_1 - \frac{3}{2}(1+6\nu)\ln\left(1+\frac{\xi}{\alpha}\right) - \frac{5}{4}(2T_1 + 1 - 2\nu)\left[1 - \frac{\alpha^2}{(\alpha+\xi)^2}\right]\right\} + o\left(\frac{\xi}{\alpha}\right) \tag{32}$$

We then obtain an expression for ϵ which is valid for small ϵ/α; that is, for D_R close to $1 + \alpha^{-1}$,

$$\epsilon = \frac{4[1 + \alpha(1 - D_R)]}{6(1+6\nu)\ln D_R + 3(2T_1 + 1 - 2\nu)(1 - D_R^{-2})} \tag{33}$$

This approximate solution predicts that ϵ approaches zero and the force becomes infinite as the draw ratio approaches a limiting value $D_R = 1 + \alpha^{-1}$. The effect of a nonzero second normal stress difference and a shear thinning viscosity is to decrease the force. Equation (31) with $T_1 = -\frac{1}{2}$ agrees with Zeichner's (1973) solution when the latter is expanded to the same order, but the value of ϵ differs by a factor of two. This is because ϵ is computed from first-order terms, some of which are neglected in Zeichner's analysis.

The nearly linear velocity profile predicted under conditions in which the imposed stress is large compared to the shear modulus is in agreement with the experimental results of Kanel (1972) and Spearot and Metzner (1972). For this linear velocity profile the strain rate γ_E, defined as dv/dz, becomes $(v_f - v_0)/L$, constant along the threadline. If α is close to $1/(D_R - 1)$ and the velocity profile is given approximately by $u = 1 + \xi/\alpha$ then we have

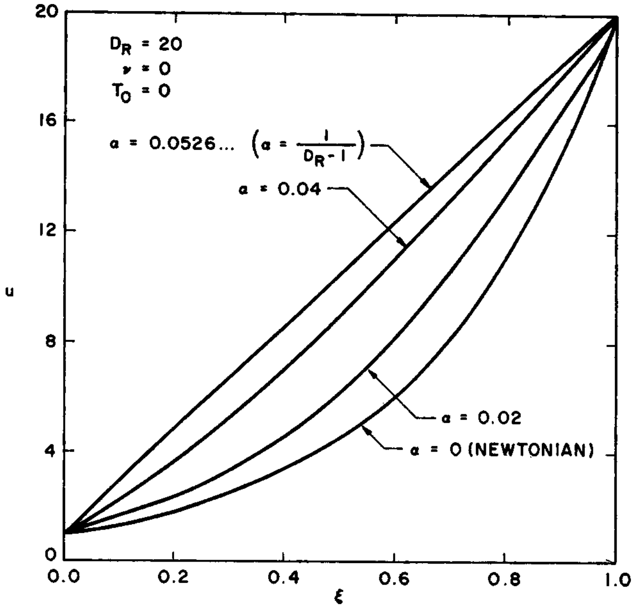

Fig. 3. Dimensionless velocity as a function of distance, $D_R = 20$, $\nu = 0$, $T_0 = 1$.

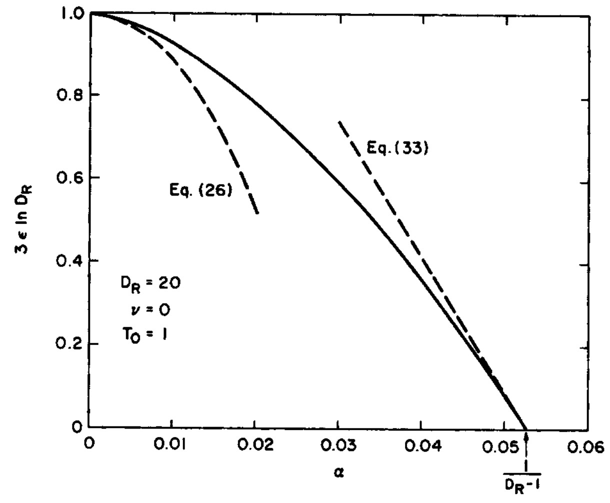

Fig. 4. Dimensionless reciprocal force as a function of viscoelastic parameter, α; $D_R = 20$, $\nu = 0$, $T_0 = 1$.

$$\lambda\gamma_E \approx \left(\frac{\alpha L}{v_0}\right)\left(\frac{v_f - v_0}{L}\right) = \left(\frac{\alpha L}{v_0}\right)\frac{v_0(D_R - 1)}{L} \approx 1$$

That is, the drawdown is accomplished in approximately one relaxation time.

NUMERICAL SOLUTION

The asymptotic solutions give considerable insight into the expected flow behavior, but the range of validity can only be established by direct numerical solution. Solutions were obtained for a range of α and T_0 using the Runge-Kutta-Gill method and the iterative procedure described above. A draw ratio of twenty is chosen for illustration because it corresponds to the limiting draw ratio which is stable to infinitesimal perturbations for a Newtonian fluid (Pearson and Matovich, 1969; Denn, 1975). Figure 3 shows some velocity profiles. Here the Newtonian result necessarily has $T(0) = 2/3$, while the results for nonzero α have $T(0) = 1$. If we plot ϵ versus α there is a curve for each value of $T(0)$, with the restriction $T(0) > 2/3 - \epsilon/\alpha$ to ensure that $du/d\xi$ is positive at $\xi = 0$. The scale in Figure 4 is normalized to the Newtonian result, $\epsilon = 1/3 \ln D_R$. If the magnitude of $T(0)$ is unrestricted there are solutions for all pairs (α, ϵ) corresponding to points below the full curve in Figure 4. Consistent with the asymptotic solutions, however, it is necessary to make $T(0)$ extremely large to alter ϵ appreciably when α is small. For larger α the restriction on $T(0)$, Equation (20), and the requirement that $\epsilon > 0$ allow a very limited range of values of $T(0)$. There is a maximum value of α at which any given draw ratio is attainable, given by Equation (30) and corresponding to $T(0) = 2/3$. The maximum value of α is achieved in the limit of infinite force $\epsilon = 0$.

The asymptotic solutions for small α (small Deborah number) and small ϵ/α (large force) are shown as dashed lines in Figure 4. The range over which the small α solution is numerically close to the computed solution is extremely small and of little practical use although the structure of the solution and the effect of the various parameters accurately reflects the complete solution. In contrast, the large force asymptotic solution with $T_1 = 0$ is in good agreement with the computed results over a wide range of allowable values of the parameter α.

COMPARISON WITH EXPERIMENT

Spearot (1972; Spearot and Metzner, 1972) has reported detailed stress and velocity profiles in ten experiments on the isothermal spinning of three low density polyethylenes, together with rheogoniometric measurements at the spinning temperatures. Spinning lengths were approximately 60 cm, with the die swell region confined to the first 2 cm. Beyond the die swell region all velocity profiles were linear within the experimental scatter, and the tensile force was nearly constant over the length of the filament. Experimentally, ϵ/α was less than 0.3. Under these conditions Equations (31) and (33) should approximately apply.

It is assumed that the rheological properties are functions only of the second invariant of the deformation rate. In simple shear this is γ_s, Equation (6d), while in a stretching flow it is $\sqrt{3}\gamma_E$. As the velocity profile becomes linear, γ_E is a constant along the length of the filament so μ, λ, and ν are true constants for the experiment. In principle, these constants can be evaluated from shear measurements for $\sqrt{3}\gamma_E = \gamma_s$.

We first attempted to predict the force from the flow rate, the rheological properties in shear, and the draw ratio. Equation (33) is extremely sensitive to small changes in λ and T_1, however, since $D_R - 1$ is close to $1/\alpha$, and meaningful results could not be obtained. For some experiments a negative value of ϵ would be computed using the shear data for λ, and this is not physically possible.

An alternative, although less satisfactory comparison, is to look upon the spinning experiment as a means of measuring λ. Equation (33) can be rearranged in the form

$$\lambda = \frac{L}{v_f - v_0}\left\{1 - \frac{3\epsilon}{2}\left[(1+6\nu)\ln D_R + \left(T_1 + \frac{1}{2} - \nu\right)(1 - D_R^{-2})\right]\right\} \quad (34)$$

Relaxation times computed from Equation (34) are shown in Figures 5 to 7, together with values obtained by Spearot from steady rheogoniometric measurements using

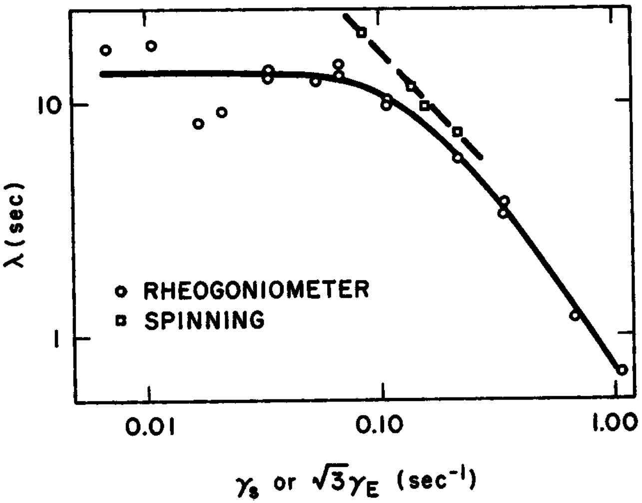

Fig. 5. Relaxation times for low density polyethylene PE-1, melt index 1.9, measured in spinning and in shear, T = 150°C. Data of Spearot (1972).

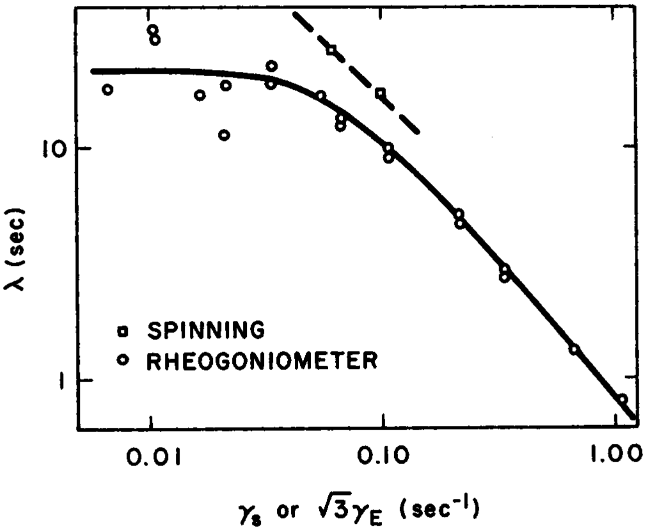

Fig. 6. Relaxation times for low density polyethylene PE-2, melt index 1.4, measured in spinning and in shear, T = 175°C. Data of Spearot (1972).

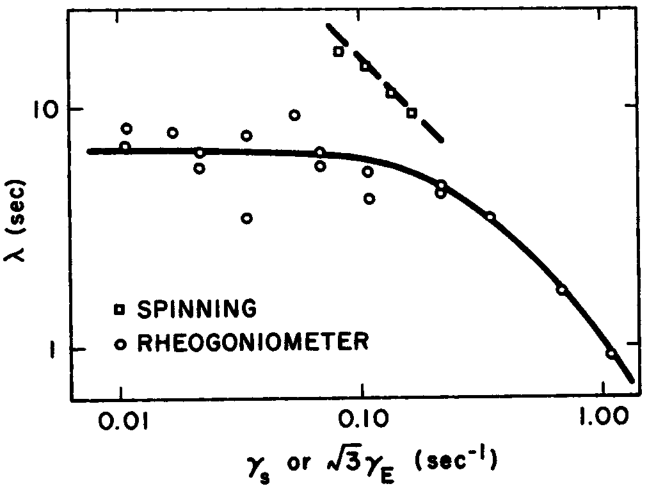

Fig. 7. Relaxation times for low density polyethylene PE-3, melt index 3.4, measured in spinning and in shear, T = 150°C. Data of Spearot (1972).

Equation (7c). The spinning relaxation times were computed with $\nu = 0$ and $T_1 = -\frac{1}{2}$, and this is effectively a lower bound on values that can be calculated from Equation (34). Values up to 10% higher are obtained by taking $\nu = -0.1$ and $T_1 = 0$. The relaxation times from the two experiments are of comparable magnitude, but those determined from steady spinning are consistently 20 to 80% larger than those determined from steady shearing.

Acierno et al. (1971) have also reported sufficiently detailed data on one experiment of the spinning of a low density polyethylene to carry out a comparable computation. In this case the spinning length was approximately six cm. The minimum value of the relaxation time computed from Equation (34) from their spinning data was 4.1 s, while they reported a largest relaxation time of 5.5 s from rheogoniometer measurements. The experimental deviation from linearity in the velocity profile is considerably greater than predicted by Equation (31) with $\lambda = 4.1$, however, and the experimental extension rate varies by a factor of three over the length of the filament. In that case a theory using constant materials parameters is unlikely to be accurate.

CONCLUSION

The theoretical analysis explains the high stress levels and nearly linear velocity profiles observed experimentally in the isothermal spinning of polymeric liquids, and it shows the nature of the smooth continuous transition from Newtonian to high Deborah number viscoelastic behavior. Given the approximate nature of the stress constitutive equation, the agreement within a factor of two between relaxation times measured in shear and in spinning must be considered quite good. It is disappointing to find, however, that the sensitivity to the relaxation time is so great that such small differences make effective prediction of the force impossible. The general tendency of the spinning relaxation times to be higher than those measured in shear is consistent with other measurements (for example, Baid, 1973). Neither the analysis nor the data are sufficiently precise to resolve the question as to whether parameters measured in shear are directly applicable to flows with extension or if the extensional kinematics affect the rheological properties.

This work points up an interesting difference between steady spinning and uniform transient extension. In uniform transient extension $\lambda\gamma_E = \frac{1}{2}$ represents a critical value in that for extension rates below this value the stress asymptotically approaches a constant in time. For higher extension rates the stress increases continuously in time. (Denn and Marrucci, 1971). In spinning there is a critical value $\lambda\gamma_E \approx 1$, for which the stresses are predicted to become infinite along the entire filament. (This difference arises essentially because the spinning experiment is carried out at constant force. The equations for uniform transient extension of a Maxwell fluid under constant force also exhibit critical behavior at $\lambda\gamma_E = 1$). It is not clear whether the restriction on $\lambda\gamma_E$ is a real one in spinning or whether it is a consequence of too simple a constitutive equation. In the experiments on low density polyethylene analyzed here, the product $\lambda\gamma_E$ was always of order unity, with a value $\lambda\gamma_E \approx 0.93$ for all experiments when λ was evaluated from the spinning experiments as described above.

The notion of a limiting stretch rate seems to be related to the establishment of the die swell region. In a free jet which is not being drawn down, the die swell occurs over a distance corresponding to several relaxation times (Metzner et al., 1966). In contrast, in the experiments of both Acierno et al. and Spearot and Metzner, in which there are large tensile stresses, the maximum die swell occurs in a small fraction of one relaxation time. It is tempting to speculate that the limit $\lambda\gamma_E < 1$ may be real, and the degree of die swell is determined at least in part by the need to establish a draw ratio satisfying $D_R \lessapprox 1.63 + 1/\alpha$.

Another way of looking at the limiting stretch rate is to take the view that however hard we pull, we cannot draw the filament down in a time less than the relaxation time λ. As the force increases without bound, however, the time in the draw region approaches λ from above. Thus, Equation (34) should not be incorrectly interpreted as implying that for large force, $\epsilon \to 0$, the fluid relaxation time $\lambda \approx L/(v_f - v_0)$ is determined independently of material properties. Rather, the equation implies that the particular material property λ determines the maximum takeup speed v_f.

It is a convenient feature of the analysis that the stress initial condition does not have an important effect on the kinematics. Again, we may think of the die swell region as a region where the stress readjusts to meet the constraints imposed on T_0 by the flow downstream.

Finally, one of the interesting results of Zeichner's analysis (1973; Denn, 1975) is the prediction of an operating region which is stable to infinitesimal disturbances at very high draw ratio. This stable high draw region corresponds to $\epsilon/\alpha \to 0$, which is precisely where Zeichner's assumption that $|T| >> |P|$ is best. Thus, it is likely that at least the qualitative conclusion of a stable high draw region is accurate, although the precise stability boundary might change somewhat.

ACKNOWLEDGMENT

M. M. Denn received support from the National Science Foundation under grant GK-43303 during the course of this work. C. J. S. Petrie received support from the Science Research Council (London) and a Leverhulme Fellowship during study leave at the University of Delaware.

NOTATION

$\mathbf{A}$ = $\nabla \mathbf{v} + (\nabla \mathbf{v})^T$
D_R = draw ratio
F = force
G = shear modulus
L = filament length
N_1, N_2 = primary, secondary normal stress difference
P = dimensionless extra stress in x-direction
Q = volumetric flow rate
T = dimensionless extra stress in z-direction
T_0 = initial value of T
T_1 = initial value of $\alpha(T - 1)/\epsilon$
u = dimensionless axial velocity
v = axial velocity component
$\mathbf{v}, v^i$ = velocity vector
v_0 = initial velocity
v_f = final velocity
x = direction normal to extension
z = axial direction

Greek Letters

α = dimensionless rheological parameter
γ_E = extension rate
γ_s = shear rate
ϵ = dimensionless reciprocal force
λ = relaxation time
μ = zero-shear viscosity
ν = zero-shear value of N_2/N_1
ξ = dimensionless axial position
$\boldsymbol{\tau}, \tau^{ij}$ = extra-stress tensor
τ_0 = initial value of τ^{zz}

$(\ )^T$ = transpose
∇ = gradient operator
$\mathfrak{d}/\mathfrak{d}t$ = Oldroyd differential operator

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Manuscript received January 2, 1975; revision received March 28 and accepted March 31, 1975.

Real-Time Time-Optimal Control of a Stirred-Tank Reactor Using Kalman Filtering for State Estimation

EDMOND B. LYNCH
and
W. FRED RAMIREZ

Department of Chemical Engineering
University of Colorado
Boulder, Colorado 80302

This paper presents the development and real-time implementation of a time-optimal control algorithm for a continuous stirred-tank reactor. A multivariable time-optimal control law is derived and an Extended Kalman Filter formuated for on-line estimation and filtering. The work demonstrates the powerful capability of real-time computation and decision-making in optimal control and optimal estimation of process states.

SCOPE

With the advent of the process computer and particularly the minicomputer, computer control is beginning to take hold in the chemical industry. Most of this computer control activity, however, has been essentially data acquisition with heavy operator intervention, or on the most sophisticated level, feedback control on isolated states of the process.

In contrast to single-loop feedback control, the implementation of optimal control demands knowledge of all the process states of the system. Although much simulation work has been done using optimal control theory and some experimental work has been demonstrated, little to date has been reported on using on-line digital optimal control for actual nonlinear systems. Thus, the motivation of this work is the development and implementation of a time-optimal control algorithm for a continuously stirred-tank reactor. The reaction studied is the decomposition of hydrogen peroxide. A General Data Corporation Nova 1210 series minicomputer with 8K words of storage was used to implement the time-optimal control policy. Also an Extended Kalman Filter is used to determine optimal estimates of the process states.

CONCLUSIONS AND SIGNIFICANCE

This paper presents a total study of on-line computer control of a chemical process. It takes a well modeled process with realistic systematic noise and measurement difficulty, and controls the process time-optimally without using large amounts of minicomputer core storage. A multivariable time optimal control law is derived and an Extended Kalman Filter formulated for on-line estimation and filtering of the process states. Simulation and experimental results show that the Kalman Filter works very well in estimating the unmeasured system states and filtering the measurement noise in the system. Simulated and experimental trajectories investigated modeling uncertainties between the actual real-time controlled system and a simulated

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Correspondence concerning this paper should be addressed to W. F. Ramirez.