General Analysis for Free Drainage of Non-Newtonian Films from Flat Plates when Inertial and Surface Tension Forces and Normal Stresses Are Negligible

General equations for (1) thickness, (2) specific holdup, and (3) specific flow rate of non-Newtonian films under conditions of plane free drainage with negligible inertial and interfacial tension forces and normal stresses as functions of position and time are derived. Use of these equations reduces the heretofore tedious process of derivation for a particular rheological model of expressions for film thickness, holdup, and flow rate to a single-step operation for film thickness and relatively simple processes for holdup and flow rate. The general equations are evaluated for popular non-Newtonian models, with description of efficient methods for doing so, and the results for thickness, holdup, and flow rate, many new, in compact dimensionless form made available to the interested reader in a supplement.

JOHN PENDERGRASS

School of Chemical Engineering
Cornell University
Ithaca, New York 14850

SCOPE

When (1) a solid object initially immersed in a liquid is withdrawn or (2) a liquid coating is applied to a solid object or (3) a vessel filled with a liquid is emptied, a film of liquid adheres to the solid surface. The film drains and thins under the influence of various forces, usually gravitational and interfacial, but with centrifugal and other inertial forces, electrical forces, etc. occasionally significant or even dominant. These three cases, referred to respectively as *unsteady withdrawal*, *film coating*, and *vessel emptying*, but categorized together as *free drainage*, are discussed, related, and illustrated in an excellent review by Tallmadge and Gutfinger (1967).

A list, by no means exhaustive, of examples of processes in which film drainage is of practical interest includes painting, electroplating, dip coating, hot tinning, pickling, lubrication, rinsing, drainage of large process vessels and scientific instruments (buret, pipet, volumetric flask, capillary viscometer, etc., drainage can be of significant influence on ultimate accuracy of use of these instruments), removal of mother liquor from crystalline solids and leaching agents from spent materials by gravity drainage and centrifugation, etc. Dragout of objectionable liquids, for example, in electroplating, can be of considerable concern to persons involved in industrial safety and protection of the environment. For many of these processes knowledge of film thickness is of primary interest. In others the ability to accurately estimate dragout or total residue and/or drainage rates may be of greater significance. In a large percentage of practical free drainage operations the fluids involved are non-Newtonian.

The principal objective of the present study was development of general methods for rapid derivation of expressions for film thickness, specific holdup, and specific volume flow rate as functions of position and time for non-Newtonian free drainage from flat solid surfaces under the influence of gravity for conditions under which inertial and interfacial tension forces and normal stresses are negligible. The analysis was to be based on a simple, but useful, model of draining film flow. A secondary objective was evaluation of the general formulas for several popular non-Newtonian models, with description of efficient methods for doing so, and presentation of specific new results for film thickness, holdup, and drainage rates in compact nondimensionless form in a Supplement to be made available to interested readers.*

The restrictions upon non-Newtonian rheological model characteristics required for applicability of the methods described herein are not severe: (1) viscoelasticity and time-dependence of physical properties are prohibited and (2) neglecting normal stresses, explicit solubility of the rheological model for the single quasi steady, quasi fully-developed velocity gradient is necessary. In particular, yield shear stress phenomena are not excluded from consideration.

The film flow model, depicted schematically in Figure 1, in addition to neglect of inertial and interfacial tension forces and constancy of physical properties, involves the following: (1) requirement that the flow be laminar and nonrippling, (2) neglect of gas-liquid interfacial shear stress, (3) approximation of the flow as quasi steady and quasi fully-developed in accordance with local and instantaneous film thickness at all times and positions, (4) neglect of effects of normal stresses on the flow, and (5) infinite extent of the film in both the horizontal and vertical directions. The general behavior expected of the draining film includes: (1) thickness initially infinite for all z for all practical purposes and (2) zero thickness at the upper edge $z = 0$ of the film following initiation of

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drainage and for all z as the time allowed for drainage becomes infinite (except when a yield shear stress is involved, in which case the film thickness at the upper edge and for infinite drainage time is given by the yield stress divided by the fluid specific weight in the direction of drainage).

This flow model should be regarded as a first-order model and a candidate for considerable refinement, for example, see Tallmadge and Gutfinger (1967). Nonetheless, predictions of free drainage behavior based on this flow model agree satisfactorily with experiment for conditions under which neglect of interfacial tension and inertial forces and normal stresses is justified. In particular, Groenveld (1971) and Gutfinger and Tallmadge (1964) indicate that all Newtonian free drainage phenomena exhibit behavior adequately predicted by analyses based on this simple flow model whenever the drainage time is sufficiently large. Furthermore, the results of analyses based on this flow model serve as starting points for more elaborate analyses of free drainage, for example, by Chase and Gutfinger (1967), Lang and Tallmadge (1971) and Tallmadge (1971). Vertical plane free drainage is, of course, also a useful approximation for vertical drainage from curved surfaces when the curvature is small.

Early analyses of free drainage for Newtonian liquids include those of Jeffreys (1930) and Van Rossum (1958). Previous analyses of non-Newtonian free drainage based on the flow model described include those of Gutfinger and Tallmadge (1965) for Ostwald-deWaele model fluids, of Gutfinger and Tallmadge (1965) and Denson (1972) for Ellis model fluids, Raghuraman (1971) for Reiner-Philippoff and Peak-McLean model fluids, and Gutfinger (1964) for Bingham plastic and Reiner-Rivlin model fluids.

These analyses for film thickness, holdup, and rate of drainage as functions of time and position involved a number of steps. The mathematical difficulties encountered in performing these steps naturally increased as mathematical complexity of rheological model increased, with progression from simple analytical solution to numerical analysis being required in part, for example, in going from the Newtonian through the Ostwald-deWaele to the Ellis model. Undoubtedly the mathematical difficulties, which appeared to preclude all but numerical solution, discouraged further effort directed toward analysis of free drainage involving more complex rheological models.

CONCLUSIONS AND SIGNIFICANCE

The objectives of the investigation, stated in the Scope, were met. The ease of derivation of expressions for film thickness, specific holdup, and specific drainage rate for particular non-Newtonian rheological models using the general methods presented is remarkable in comparison with previously reported analyses. The heretofore tedious process of derivation is reduced to a single-step operation for film thickness and relatively simple processes for holdup and flow rate. A dimensional analysis of the general formulas derived herein involved principles which may prove more widely useful in evaluation of general theories for large numbers of specific non-Newtonian rheological models and in ready comparison of results for the different rheological models and their compact presentation. The solution of the fundamental general differential equation describing the film drainage using similarity transform analysis emphasized the special character of the solution.

Particular results of evaluation of the general formulas, in the form of compact, nondimensional equations and graphs, for the Cassonian, Eyring hyperbolic sine, Sisko, Meter, and Reiner's structural stability rheological models are believed to be entirely new. These results appear partly in the Appendix as examples of application of the general methods developed herein and partly in a Supplement available to the interested reader. Previously published results of conventional analyses for the Newtonian, Ostwald-deWaele, Ellis, Bingham plastic, Reiner-Philippoff, Peak-McLean, and Reiner-Rivlin models are made available in the same Appendix and Supplement in the same new format in order to provide a complete list of currently available solutions for free drainage of the type analyzed, to allow ready comparison of the solutions, and to present some new results for some of this latter group of models.

The general methods and specific solutions presented should facilitate mathematical modeling and simulation of free drainage phenomena for non-Newtonian liquids and may lead to the use of free drainage experiments for determination of appropriate rheological models for non-Newtonian fluids and for rheological parameter estimation. Difficulties encountered in attempts to use the same general approach for analysis of drainage from sharply curved vertical surfaces and from nonvertical surfaces of any degree of curvature are pointed out. An extensive discussion of conditions for which descriptions of the type developed herein for free drainage are expected to be of adequate accuracy is also presented in the Supplement to be made available to the interested reader.

GENERAL ANALYSIS

Film Thickness

The film flow model adopted for analysis involves but a single non-negligible quasi steady and quasi fully-developed velocity gradient and shear stress component. The shear stress distribution is given as a function of position normal to the solid surface by

$$\tau_{xz}(x) = (\rho_L - \rho_V) g \cos(\beta) x = \phi_\beta x, \quad 0 \leq x \leq \delta(z, t) \tag{1}$$

To emphasize the quasi steady, quasi fully-developed nature of the flow model, dependence of shear stress and velocity distributions on position and time are indicated only through denoting dependence of film thickness on position and time. The listed restrictions on non-Newtonian rheological model characteristics imply reduction of the rheological model to the form:

$$\frac{dv_z(x)}{dx} = \begin{cases} 0, & 0 \leq \tau_{xz}(x) \leq \tau_0 \\ -f(\tau_{xz}(x)), & \tau_0 \leq \tau_{xz}(x) \leq \tau_{xz}(\delta(z,t)) \end{cases} \tag{2}$$

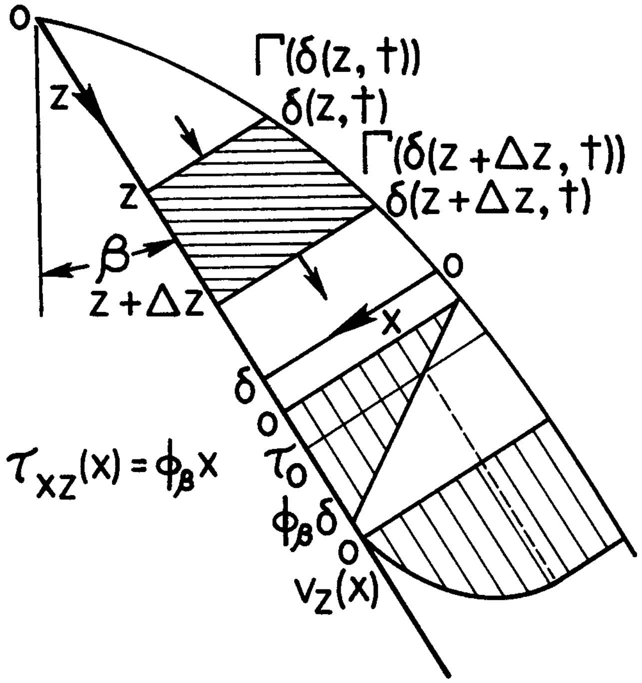

Fig. 1. Schematic of film flow model.

with yield shear stress taken explicitly into consideration for the simple flow model being analyzed.

The shear stress distribution may be substituted into the general rheological model to get

$$\frac{dv_z(x)}{dx} = \begin{cases} 0, & 0 \leq x \leq \tau_0/\phi_\beta \\ -f(\phi_\beta x), & \tau_0/\phi_\beta \leq x \leq \delta(z,t) \end{cases} \tag{3}$$

The quasi steady, quasi fully-developed velocity distribution is obtained by integration

$$v_z(x) = \begin{cases} \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta x)\,dx, & 0 \leq x \leq \tau_0/\phi_\beta \\ \int_x^{\delta(z,t)} f(\phi_\beta y)\,dy, & \tau_0/\phi_\beta \leq x \leq \delta(z,t) \end{cases} \tag{4}$$

and satisfaction of the condition

$$v_z(x) = 0, \quad x = \delta(z,t) \tag{5}$$

A second integration yields the quasi steady, quasi fully-developed specific (per unit width of flow path) volume flow rate for the draining film:

$$\Gamma(\delta(z,t)) = \int_0^{\delta(z,t)} v_z(x)\,dx$$

$$= \tau_0/\phi_\beta \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta x)\,dx + \int_{\tau_0/\phi_\beta}^{\delta(z,t)} \left[\int_x^{\delta(z,t)} f(\phi_\beta y)\,dy\right] dx \tag{6}$$

A mass balance on an element of draining film, depicted schematically in Figure 1:

(net rate of accumulation of mass within element)

+ (net rate of convection of mass from element) = 0 (7)

may be expressed as

$$\rho_L \frac{\partial \delta(z,t)}{\partial t} \Delta z + \dot{m}(z + \Delta z, t) - \dot{m}(z,t) = 0 \tag{8}$$

Taking limits as Δz approaches zero results in a continuity equation for the draining film:

$$\rho_L \frac{\partial \delta(z,t)}{\partial t} + \frac{\partial \dot{m}(z,t)}{\partial z} = 0 \tag{9}$$

But

$$\dot{m}(z,t) = \rho_L \Gamma(\delta(z,t)) \tag{10}$$

and therefore

$$\frac{\partial \dot{m}(z,t)}{\partial z} = \rho_L \frac{\partial \Gamma(\delta(z,t))}{\partial z} = \rho_L \frac{\partial \Gamma(\delta(z,t))}{\partial \delta(z,t)} \frac{\partial \delta(z,t)}{\partial z} \tag{11}$$

The Leibnitz formula

$$\frac{d}{dx}\left[\int_{a(x)}^{b(x)} F(x,t)\,dt\right] = F(x, b(x))\frac{db(x)}{dx} - F(x, a(x))\frac{da(x)}{dx} + \int_{a(x)}^{b(x)} \frac{\partial F(x,t)}{\partial x}\,dt \tag{12}$$

for differentiation of an integral with variable limits can be used to evaluate the derivative of specific volume flow rate with respect to film thickness:

$$\frac{d\Gamma(\delta(z,t))}{d\delta(z,t)} = \delta(z,t) f(\phi_\beta \delta(z,t)) \tag{13}$$

Substitution of Equations (11) and (13) into the film continuity equation gives

$$\frac{\partial \delta(z,t)}{\partial t} + \delta(z,t) f(\phi_\beta \delta(z,t)) \frac{\partial \delta(z,t)}{\partial z} = 0 \tag{14}$$

or more succinctly

$$\frac{\partial \delta}{\partial t} + \delta f(\phi_\beta \delta) \frac{\partial \delta}{\partial z} = 0 \tag{15}$$

Now consider the introduction of the similarity variable:

$$\lambda = z/t \tag{16}$$

into the final form, Equation (15), of the film continuity equation according to

$$\frac{\partial \delta}{\partial t} = \frac{d\delta}{d\lambda}\frac{\partial \lambda}{\partial t} = -\frac{z}{t^2}\frac{d\delta}{d\lambda} = -\frac{1}{t}\frac{d\delta}{d\lambda},$$

$$\frac{\partial \delta}{\partial z} = \frac{d\delta}{d\lambda}\frac{\partial \lambda}{\partial z} = \frac{1}{t}\frac{d\delta}{d\lambda} \tag{17}$$

to arrive at

$$[-\lambda + \delta f(\phi_\beta \delta)]\frac{d\delta}{d\lambda} = 0 \tag{18}$$

But

$$\frac{d\delta}{d\lambda} \neq 0 \tag{19}$$

in general, and the inescapable conclusion is that

$$-\lambda + \delta f(\phi_\beta \delta) = 0 \tag{20}$$

or:

$$\delta f(\phi_\beta \delta) = \lambda = z/t \tag{21}$$

Similarity analysis has apparently not been previously used in analyzing free drainage. In addition, the application of similarity analysis to a first-order partial differential equation with the unusual outcome obtained above appears to have not been previously reported. It should, however, be noted that the use of similarity analysis excludes from consideration an infinity of solutions to Equation (15). These other solutions, associated with more elaborate auxiliary conditions, are not required for present purposes.

It is clear that given a rheological model in proper form one can write down in a single step the relationship between film thickness, position, and time. The general formula, of course, yields previously reported solutions by Jeffreys (1930) for the Newtonian model, by Gutfinger and Tallmadge (1965) for the Ostwald-deWaele and Ellis models, by Raghuraman (1971) for the Reiner-Philippoff and Peak-McLean models, and by Gutfinger (1964) for the Bingham plastic and Reiner-Rivlin models. In addition, it predicts film drainage behavior expected for physically realistic rheological models. In particular, physically realistic models possess the mathematical properties:

$$\lim_{\delta \to \tau_0/\phi_\beta} [f(\phi_\beta \delta] = 0, \quad \lim_{\delta \to \infty} [f(\phi_\beta \delta)] = \infty \qquad (22)$$

and for such rheological models the fundamental equation exhibits the mathematical properties:

$$\lim_{\lambda \to 0} [\delta] = \tau_0/\phi_\beta, \quad \lim_{\lambda \to \infty} [\delta] = \infty \qquad (23)$$

The ease of analysis for film thickness as a function of position and time using the general formula derived herein will now be contrasted with that of the direct approach which appears to have been used in all previously published analyses of free drainage of the type under consideration. The direct approach involves many of the steps used in deriving the general formula:

1. Prior selection of a particular rheological model: If investigations using more than one rheological model were to be performed, the entire direct analysis had to be repeated for each rheological model.

2. Integration of a first-order, variable-separable, ordinary differential equation for the quasi steady, quasi fully-developed velocity distribution: Although the differential equation is of elementary type, analytical integration becomes increasingly difficult as rheological model complexity increases, for example, the progression from Newtonian through Ostwald-deWaele to Ellis models, and eventually becomes impossible, for example, Sisko and Meter models, except for special parameter values.

3. Integration of a first-order, variable-separable, ordinary differential equation for the quasi steady, quasi fully-developed specific volume flow rate, with similar problems with analytic integration.

4. Differentiation of the specific volume flow rate expression with respect to film thickness and insertion of the result into the film continuity equation.

5. Integration of the first-order partial differential equation resulting from the preceding step: The integration was first accomplished by guessing the form of the solution (Jeffreys, 1930) and later by application of basic theory of partial differentiation and integration (Van Rossum, 1958). Similarity transform analysis does not appear to offer significant advantage over the methods of Van Rossum, but may be easier to accept by the mathematically unsophisticated and does emphasize the special nature of the particular solution of the partial differential equation satisfying the listed conditions.

The new method of analysis requires but a single step for determination of film thickness as a function of position and time and, as demonstrated in the next section, single integrations for specific holdup and volume flow rate, with further economies possible if both holdup and volume flow rate are to be determined. The ease of analysis resulting from application of the general formulas will facilitate the use of experimental data on film thickness as a function of position and time for deduction of appropriate rheological models for non-Newtonian liquids and determination of rheological parameter values for the type of flow conditions involved in free drainage of films. Using the direct approach described above, rapid trial of distinct families of rheological models would not be feasible, while the new methods, of course, permit this. Simulation of more complex film drainage processes, for example, also involving heat and/or mass transfer, for which the film drainage model used in the present study remains adequate, is also facilitated.

Unfortunately, the general methods of analysis for flat plate drainage cannot be applied intact to analysis of vertical curved surfaces of non-negligible curvature, for example, from a vertical cylinder of small radius. The principal difficulty arises from the fact that the quasi steady, quasi fully-developed shear stress distribution is a direct function of the film thickness. Substitution into the rheological model results in the velocity gradient function having both radial position and film thickness as arguments. Therefore, the derivative of specific volume flow rate with respect to film thickness cannot be determined for an unspecified rheological model. Thus the stage of analysis for flat plate drainage represented by Equation (13) cannot be performed for vertical curved surface drainage for unspecified rheological model. For nonvertical curved surfaces the same problem arises and, in addition, the flow is considerably more complex, that is, no longer quasi one dimensional.

Film Specific Volume or Holdup and Volume Flow Rate

The specific (per unit width of flow path) volume contained in the draining film at any time t between the upper edge of the film and any position z is often easily obtained using the following approach. By definition:

$$V(z, t) = \int_0^z \delta(z, t)\, dz \qquad (24)$$

The direct evaluation of the defining integral appears to have been used exclusively in previous published work. But as previously deduced

$$\delta f(\phi_\beta \delta) = z/t \qquad (25)$$

and therefore for fixed time

$$dz = t \frac{d}{d\delta} [\delta f(\phi_\beta \delta]\, d\delta \qquad (26)$$

Hence one may rewrite the defining integral as

$$V(z, t) = t \int_{\tau_0/\phi_\beta}^{\delta(z,t)} \frac{d}{d\delta} [\delta f(\phi_\beta \delta)]\, d\delta \qquad (27)$$

Integration of this latter form by parts is frequently helpful and, as will be seen subsequently, aids in deducing a relationship involving specific holdup, specific flow rate, film thickness, position, and time. Thus,

$$V(z, t) = t[\delta^2 f(\phi_\beta \delta)]_{\tau_0/\phi_\beta}^{\delta(z,t)} - t \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta \delta)\, d\delta$$

$$= t\delta^2(z, t) f(\phi_\beta \delta(z, t)) - t \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta \delta)\, d\delta \qquad (28)$$

if it is recalled that

$$f(\tau_0) = 0 \qquad (29)$$

Equations (27) and (28) are, of course, of greatest utility when the fundamental equation, Equation (21), cannot be solved explicitly for δ as a function of z and t.

If this is the case then analytic evaluation of the definition, Equation (24), is, of course, impossible. Equations (27) and (28) may or may not be integrable analytically, but even if their integration must be performed numerically the effort involved will generally be less. Numerical evaluation of the defining integral requires at least one solution of an implicit equation at each integration step, in addition to application of the numerical integration formula, while numerical evaluation of the integrals of Equations (27) and (28) requires only function evaluations and application of an integration algorithm. However, the results of evaluations of Equations (27) and (28) are in terms of δ rather than the often preferred z and t. To obtain results in terms of these two variables solution of the implicit fundamental equation is necessary. Generally, however, the number of implicit equation solutions required in a particular case will be much less than the number required for integration of the defining integral and occasionally results in terms of film thickness are preferable. In addition, instances in which analytic analysis is more easily accomplished by integration of one of Equations (27) and (28) followed by substitution of the fundamental equation may arise. Finally, it should also be borne in mind that if a yield shear stress is not a feature of the rheological model then the lower limit of integration in both Equations (27) and (28) is zero.

Similarly, the specific (per unit width of flow path) volume flow rate within the film as a function of position z and time t is frequently most readily obtained in the following manner. One can, of course, evaluate the defining equation

$$\Gamma(z,t) = \int_0^{\delta(z,t)} v_z(x)\,dx$$

$$= \tau_0/\phi_\beta \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta x)\,dx + \int_{\tau_0/\phi_\beta}^{\delta(z,t)} \left[\int_x^{\delta(z,t)} f(\phi_\beta y)\,dy\right] dx \quad (30)$$

as appears to have been the approach used previously in obtaining published results. Once again it should be noted that if the rheological model does not involve a yield shear stress then the lower limits of integration in which τ_0 appears are zero.

But as previously demonstrated,

$$\frac{d\Gamma(z,t)}{d\delta} = \delta f(\phi_\beta \delta) \quad (31)$$

and therefore

$$\Gamma(z,t) = \int_{\tau_0/\phi_\beta}^{\delta(z,t)} f(\phi_\beta \delta)\,d\delta \quad (32)$$

The evaluation of Γ in terms of δ allows the replacement of a double integration by a single integration. Either approach requires solution of the fundamental equation, Equation (21), for δ for those values of z and t for which values of Γ are required. These remarks apply if one is interested solely in evaluation of Γ to the exclusion of V. If V is also to be determined, then Γ can be easily deduced by comparing Equations (28) and (32) and noting that

$$\Gamma = \delta^2 f(\phi_\beta \delta) - V/t = \delta\lambda - V/t \quad (33)$$

The viewpoint may, of course, be reversed to that of computing V given Γ:

$$V = t\delta^2 f(\phi_\beta \delta) - t\Gamma = t\delta\lambda - t\Gamma \quad (34)$$

DIMENSIONAL ANALYSIS

The results presented to this point are applicable to any rheological model which does not violate the listed restrictions. In order to present particular results for a large number of specific rheological models in a compact, nondimensional form, further analysis is confined to rheological models which involve a viscosity or viscosity-like parameter μ^* and shear stress or shear stress-like parameter τ^* or may reasonably be cast into that form. Many rheological models are designed to describe with reasonable accuracy the approach to Newtonian behavior at low shear rates exhibited by many non-Newtonian fluids and accomplish this goal by inclusion of a Newtonian term, of course involving a viscosity-like parameter, together with terms which become negligible in comparison with the Newtonian term as shear rate goes to zero. Other viscosity-like parameters are also frequently encountered, for example, in models designed to describe an approach to Newtonian behavior at high shear rates or as features of models involving a yield stress. Examples include the Ellis model, Reiner's structural stability model, and the Bingham plastic model, respectively.

Similarly, many non-Newtonian rheological models contain a shear stress-like parameter, for example, a yield shear stress or a parameter reflecting some important mathematical characteristic of a rheological model and required to possess the dimensions of a shear stress. Respective examples include the Bingham plastic model and the Ellis model. In addition, numerous non-Newtonian rheological parameters may reasonably be interpreted as combinations of viscosity-like and shear stress-like parameters. If it is further realized that viscosity-like and shear stress-like parameters may be defined arbitrarily and inserted wherever desirable, it is readily perceived that no real restriction on the range of rheological models to be dealt with has been called for.

In addition to compactness of presentation of results, other benefits result from the strategy adopted. There is, of course, a reduction of the effort required for deduction of appropriate sets of dimensionless variables, which will, in general, be different for different rheological models if selected without some guiding principle. Furthermore, the use of the same basic set of dimensionless groups for all evaluations of the general equations for particular rheological models facilitates comparison of the results. However, it also should be realized that the common set

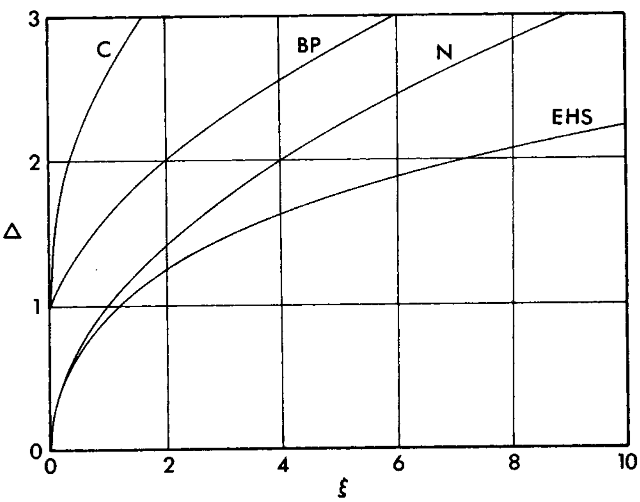

Fig. 2. Dimensionless film thickness as a function of dimensionless similarity variable for Newtonian, Bingham plastic, Cassonian, and Eyring hyperboic sine models (N, BP, C, and EHS, respectively).

of dimensionless variables may not be the most convenient for all purposes, for example, it may be deemed desirable to focus attention on a particular rheological parameter by isolating it from other rheological parameters in a special dimensionless group. Nonetheless, if a solution for a particular rheological model is available a change from one dimensionless representation to another is a trivial matter. The set of dimensionless groups listed below appears to give minimal representations except when arbitrary viscosity-like and/or shear stress-like parameters must be introduced, thereby raising the number of rheological parameters.

The core set of dimensionless variables and parameters is

(1) a dimensionless film thickness

$$\Delta = \phi_\beta \delta / \tau^* \tag{35}$$

(2) a dimensionless similarity variable

$$\xi = \mu^* \phi_\beta z / \tau^{*2} t \tag{36}$$

(3) a dimensionless specific film holdup

$$\Phi = \mu^* \phi_\beta^2 V / \tau^{*3} t \tag{37}$$

(4) a dimensionless specific film volume flow rate

$$G = \mu^* \phi_\beta^2 \Gamma / \tau^{*3} \tag{38}$$

(5) a dimensionless rheological model function:

$$F(\Delta) = \frac{\mu^*}{\tau^*} f(\phi_\beta \delta) \tag{39}$$

For rheological models involving essential parameters in addition to μ^* and τ^* one additional dimensionless parameter will be required for each additional essential parameter. Additional required dimensionless parameters have not been assigned special symbols, but have been left in explicit form.

The important Equations (21), (28), (32), and (34) cast into dimensionless form using the listed set of dimensionless groups are, respectively,

$$\Delta F(\Delta) = \xi \tag{40}$$

$$\Phi = \Delta^2 F(\Delta) - \int_{\tau_0/\tau^*}^{\Delta} \Delta F(\Delta) d\Delta \tag{41}$$

$$G = \int_{\tau_0/\tau^*}^{\Delta} \Delta F(\Delta) d\Delta \tag{42}$$

$$\Phi = \Delta \xi - G \tag{43}$$

If τ_0 is taken as τ^* then the lower limits of integration are one.

At this point, it has become evident that numerical solutions for Δ, Φ, and G as functions of ξ may be obtained without explicit solution of the dimensionless form of the fundamental equation, Equation (40), for Δ as a function of ξ. Note that ξ, Φ, and G are represented as explicit functions of Δ in Equations (40) to (43). Substitution of values for Δ into these three equations yields corresponding values for ξ, Φ, and G, from which graphs of Δ, Φ, and G as functions of ξ may be prepared if desired. Of course, numerical integration may still be necessary in order to obtain the values for Φ and G and, in general, the values of ξ for which the computations are conducted cannot be preselected.

The Appendix is devoted to examples of evaluation of the general dimensionless formulas, Equations (40) to (43), for specific rheological models. The results presented are equations for $F(\Delta)$, Δ, Φ, and G and graphs

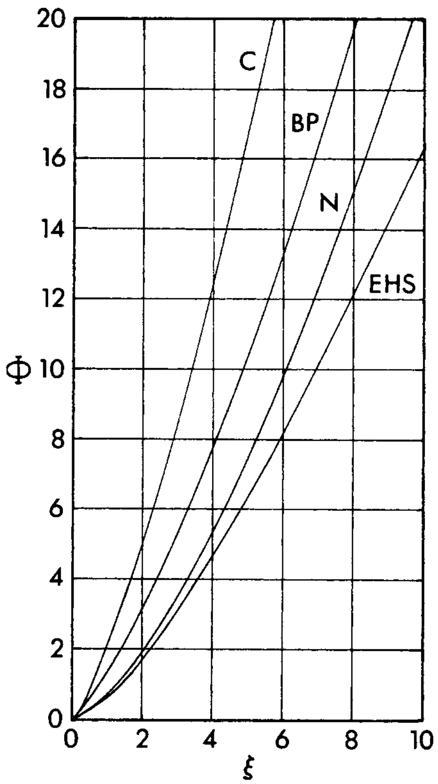

Fig. 3. Dimensionless specific film holdup as a function of dimensionless similarity variable for Newtonian, Bingham Plastic, Cassonian, and Eyring hyperbolic sine models (N, BP, C, and EHS, respectively).

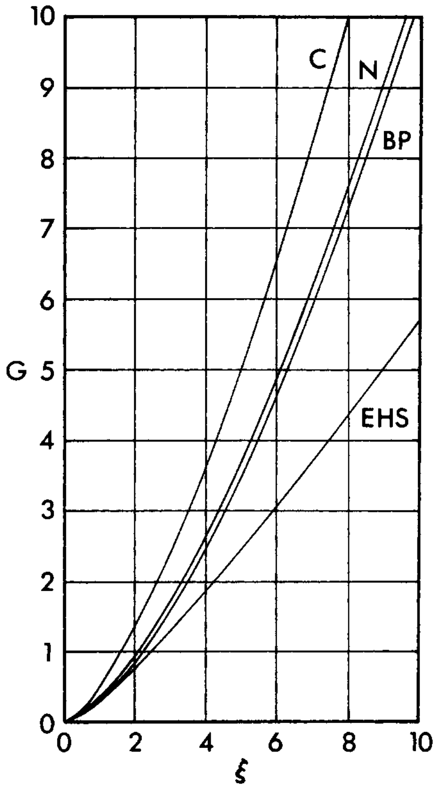

Fig. 4. Dimensionless specific film volume flow rate as a function of dimensionless similarity variable for Newtonian, Bingham plastic, Cassonian, and Eyring hyperbolic sine models (N, BP, C, and EHS, respectively).

of Δ, Φ, and G as functions of ξ. The identifications of rheological parameters with μ^* and τ^* are indicated. For those rheological models for which explicit solution for Δ as a function of ξ is possible, Φ and G are listed as explicit functions of ξ as well as functions of Δ. Presentation of previously reported solutions for the Newtonian and Bingham plastic models in this new format is believed to be new. Rheological models for which solutions presented in this Appendix are believed to be entirely new are the Cassonian and Eyring hyperbolic models.

A Supplement to the Appendix, which is available to the interested reader, is devoted to completing the presentation of available solutions to the free drainage problem considered herein. The compact nondimensional form of the presentation allows ready comparison of solutions for different rheological models. Previously reported solutions, together with a few new results, for the Ostwald-deWaele, Ellis, and Reiner-Rivlin models and the Reiner-Philippoff and Peak-McLean models as special cases of the Meter model are presented in the new format. Also listed are solutions, believed to be entirely new, for the Sisko, general Meter, and Reiner's structural stability models. An extensive examination of the conditions under which the solutions listed in the Appendix and the Supplement are expected to be useful is also presented in the Supplement.

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NOTATION

A = shear stress-like parameter, Eyring hyperbolic sine model, Appendix (IV), $ML^{-1}\theta^{-2}$
B = rheological parameter, Eyring hyperbolic sine model, Appendix (IV), θ^{-1}
f = function, Equation (2), θ^{-1}
F = dimensionless form of function f, Equation (39)
g = acceleration of gravity, $L\theta^{-2}$
G = dimensionless specific volume flow rate, Equation (38)
$\dot{m}$ = specific mass flow rate, $ML^{-1}\theta$
t = time, θ
v_z = fluid velocity in z-direction, $L\theta^{-1}$
V = specific holdup, L^2
x = coordinate normal to flat plate, Figure 1, L
y = dummy variable for x, L
z = coordinate in direction of film drainage, Figure 1, L

Greek Letters

β = angle of inclination of solid surface to the vertical, Figure 1, dimensionless
Γ = specific volume flow rate, $L^2\theta^{-1}$
δ = film thickness, L
Δ = dimensionless film thickness, Equation (35)
η_c = viscosity-like parameter, Cassonian model, Appendix (III), $ML^{-1}\theta^{-1}$
λ = similarity variable, Equation (16), $L\theta^{-1}$
μ = Newtonian viscosity, $ML^{-1}\theta^{-1}$
μ_0 = viscosity-like parameter, Bingham plastic model, Appendix (II), $ML^{-1}\theta^{-1}$
μ^* = viscosity-like parameter, $ML^{-1}\theta^{-1}$
ξ = dimensionless similarity variable, Equation (36)
ρ_L = liquid density, ML^{-3}
ρ_V = vapor density, ML^{-3}
τ_{xz} = shear stress in z-direction per unit area normal to x-direction, $ML^{-1}\theta^{-2}$
τ^* = shear stress-like parameter, $ML^{-1}\theta^{-2}$
τ_0 = yield shear stress, general, Bingham plastic, Cassonian models, Equation (2), Appendix (II, III), $ML^{-1}\theta^{-2}$
ϕ_β = specific weight of film in z-direction, Equation (1), $ML^{-2}\theta^{-2}$
Φ = dimensionless specific holdup, Equation (37)

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APPENDIX: EVALUATION OF GENERAL FORMULAS FOR SPECIFIC NON-NEWTONIAN RHEOLOGICAL MODELS

(I) Newtonian model:

$$f(\tau_{xz}) = \tau_{xz}/\mu, \quad \mu > 0$$

$\mu = \mu^*$, arbitrary τ^* introduced

$$F(\Delta) = \Delta$$

$$\Delta = \xi^{1/2} \qquad \text{(See Figure 2)}$$

$$\Phi = \frac{2}{3}\Delta^3 = \frac{2}{3}\xi^{3/2} \qquad \text{(see Figure 3)}$$

$$G = \frac{1}{3}\Delta^3 = \frac{1}{3}\xi^{3/2} \qquad \text{(see Figure 4)}$$

(II) Bingham plastic model (Bird et al., 1960):

$$f(\tau_{xz}) = \left\{ \begin{array}{ll} 0, & \tau_{xz} \leqq \tau_0 \\ (\tau_{xz} - \tau_0)/\mu_0, & \tau_{xz} \geqq \tau_0 \end{array} \right\}, \quad \mu_0 > 0, \quad \tau_0 \geqq 0$$

$\mu_0 = \mu^*$, $\tau_0 = \tau^*$

$$F(\Delta) = \Delta - 1$$

$$\Delta = \frac{1 + (1 + 4\xi)^{1/2}}{2} \qquad \text{(see Figure 2)}$$

$$\Phi = \frac{2}{3}\Delta^3 - \frac{1}{2}\Delta^2 - \frac{1}{6}$$

$$= \frac{2}{3}\left[\frac{1+(1+4\xi)^{1/2}}{2}\right]^3 - \frac{1}{2}\left[\frac{1+(1+4\xi)^{1/2}}{2}\right]^2 - \frac{1}{6} \quad \text{(see Figure 3)}$$

$$G = \frac{1}{3}\Delta^3 - \frac{1}{2}\Delta^2 + \frac{1}{6}$$

$$= \frac{1}{3}\left[\frac{1+(1+4\xi)^{1/2}}{2}\right]^3 - \frac{1}{2}\left[\frac{1+(1+4\xi)^{1/2}}{2}\right]^2 + \frac{1}{6} \quad \text{(see Figure 4)}$$

(III) Cassonian model (Kooijman and Van Zanten, 1972):

$$f(\tau_{xz}) = \begin{cases} 0, & \tau_{xz} \leqq \tau_C \\ (\tau_{xz}^{1/2} - \tau_C^{1/2})^2/\eta_C, & \tau_{xz} \geqq \tau_C \end{cases}, \quad \eta_C > 0, \quad \tau_C \geqq 0$$

$$\eta_C = \mu^*, \quad \tau_C = \tau^*$$

$$F(\Delta) = (\Delta^{1/2} - 1)^2$$

$$\Delta(\Delta^{1/2} - 1)^2 = \xi \quad \text{(see Figure 2)}$$

$$\Phi = \frac{2}{3}\Delta^3 - \frac{6}{5}\Delta^{5/2} + \frac{1}{2}\Delta^2 + \frac{1}{30} \quad \text{(see Figure 3)}$$

$$G = \frac{1}{3}\Delta^3 - \frac{4}{5}\Delta^{5/2} + \frac{1}{2}\Delta^2 - \frac{1}{30} \quad \text{(see Figure 4)}$$

(IV) Eyring hyperbolic sine model (Bird et al., 1960):

$$f(\tau_{xz}) = B\sinh(\tau_{xz}/A), \quad A > 0, \quad B > 0$$

$A = \tau^*$, B interpreted as τ^*/μ^*

$$F(\Delta) = \sinh(\Delta)$$

$$\Delta\sinh(\Delta) = \xi \quad \text{(see Figure 2)}$$

$$\Phi = \Delta^2\sinh(\Delta) - \Delta\cosh(\Delta) + \sinh(\Delta) \quad \text{(see Figure 3)}$$

$$G = \Delta\cosh(\Delta) - \sinh(\Delta) \quad \text{(see Figure 4)}$$

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Effects of Nonseparable Kinetics in Alcohol Dehydration over Poisoned Silica-Alumina

Methanol and ethanol dehydration over fresh and poisoned silica-alumina have been used as a model system to demonstrate experimentally certain effects of nonseparable kinetics including the change in product distribution upon flow reversal in a reactor with a poisoning gradient. The rate expression $r = kK_Ac_A^{1/2}/(1 + K_Ac_A^{1/2} + K_Wc_W)$ describes the experimental data for all reactions although the constants for ether and olefin formation are entirely different and vary between fresh and poisoned catalysts. The nonseparability of kinetics and the concomitant variation of K_A, K_W with poisoning are briefly discussed in terms of interactions between poison molecules and surface acid-base sites.

K. R. BAKSHI
and
G. R. GAVALAS
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

SCOPE

A variety of deactivation processes including sintering, coking, and poisoning necessitate periodic catalyst replacement or regeneration. Between regenerations the catalyst is subject to continuous change inducing a change in the product distribution and posing problems of optimal operation and regeneration. Such optimization problems require models describing the kinetics on partially poisoned catalysts. For the sake of simplicity and due to the lack of detailed information, the kinetic models employed heretofore have been of the separable type. A separable kinetic model has the form $r = \phi r_i$, where r_i is an intrinsic rate, independent of poison adsorption, and ϕ is a factor accounting for the effect of the poison. Although separable kinetics does not explain changes in selectivity, it has been considered suitable for engineering calculations.

In a previous paper Gavalas (1971) has shown by computer simulation that separable kinetics fails to describe some important effects, such as the dependence of product distribution upon the direction of flow through a reactor with a poisoning gradient. This flow-directional effect and other related effects can be exploited in actual reactor operation to optimize the overall product distribution between successive regenerations. The purpose of this paper is to give an experimental demonstration of the flow-directional effect and other implications of nonseparable kinetics, using alcohol dehydration on acidic catalysts as a model system.

Correspondence concerning this paper should be addressed to G. R. Gavalas. K. R. Bakshi is with Chevron Research Company, Richmond, California 94802.