RESIDENCE TIME DISTRIBUTION IN LAMINAR FLOW SYSTEMS.II.* NON-NEWTONIAN TUBULAR FLOW

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The finite part of a tube of a circular cross-section is investigated being considered a continuous laminar flow system with developed velocity profile and no mass transport by molecular diffusion. General relationships derived are being applied for an isothermal non-Newtonian flow for which the residence time distribution function is linked with the viscosity function of the liquid concerned. Asymptotic and limit properties of distribution functions have been studied simultaneously with functional properties of viscosity function which influence the former. A comparison of normalized distribution functions is given for various rheological models of viscosity function using the concept of pseudosimilarity. Further, an attempt has been made to interpret the distribution functions be means of generalized formulae based upon the asymptotic and limit behaviour of distribution functions.

The only continuous flow system for which the hydrodynamic approach[1] to the residence time distribution has been applied is the developed steady tubular laminar flow. This approach has been applied so far for problems of axial dispersions[2,3] and for tubular chemical reactors[4,5]. In the latter ones, the non-Newtonian behaviour was also taken into consideration. This was possible only because the assumption of the negligible role of molecular transport compared with the laminar convective transport is particularly well fulfilled for the flows of highly viscous liquids and suspensions which are very often of a non-Newtonian character. The conclusions of the papers[4,5] are limited, however, for the case when viscosity function can be interpreted by the power law

$$-\,\mathrm{d}v/\mathrm{d}r = D[\tau] = (\tau/K)^{1/n}\,, \qquad (1)$$

which is applicable, of course, only in a limited range of variables τ and D.

The aim of this analysis is to test and interpret the conclusions of our previous analysis[1] for a relatively simple case, investigate the residence time distribution functions for non-Newtonian laminar tubular flows without the limitations of the "power-law" behaviour, estimate the extent of applicability of the results obtained for the "power-law" behaviour[4,5] in cases where the power-law fails to interpret the viscosity function of the liquid concerned.

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KINEMATICS OF TUBULAR FLOW

The kinematics of a fully developed laminar tubular flow is entirely characterised by the radial profile of axial velocities, $v = v(r)$. The distribution function of residence times is therefore determined by the velocity profile in the way discussed in the first part of our analysis[1]. Let us limit the finite section of a tube of the length L by two planes $z = 0$ and $z = L$ in the region of a fully developed laminar flow (Fig. 1). In this case, the streamlines are straight lines φ = const, r = const. Because of the axial symmetry, the transit times of liquid elements along all streamlines of the radius r are identical. The transit time ϑ through the tube section Lalong the streamline of the radius r is obviously given by

$$\vartheta = \vartheta(r) = L/v(r) . \tag{2}$$

where $v(r)$ is the point velocity.

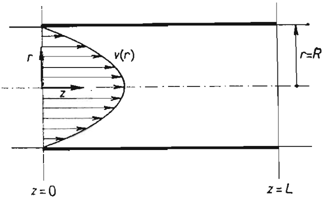

FIG. 1
Sketch of the Tubular Flow

The circle the centre of which is $r = 0$ and the radius of which is r_t represents the part of the outlet area through which there is a flow of that portion of the liquid having the transit time equal to or shorter than $t = L/v(r)$. The volumetric flow rate through this area is then given by

$$Q_t = Q(r_t) = \int_0^{r_t} v(r)\, 2\pi r\, \mathrm{d}r \tag{3a}$$

or in the form[6]

$$Q_t = v(r_t)\, \pi r_t^2 + \int_0^{r_t} (-\mathrm{d}v/\mathrm{d}r)\, \pi r^2\, \mathrm{d}r . \tag{3b}$$

The distribution function of residence times $F(t)$, which gives the fraction of the liquid passing the system in a time shorter than or equal to t, can be expressed as a ratio of the volumetric flow rate Q_t and the overall rate $Q = Q(R)$. Thus the distribution function of residence times can be presented in a parametric form[2,4] as

$$F = Q(r_t)/Q\,, \quad t = \vartheta(r_t) = L/v(r_t) . \tag{4a, b}$$

In applications, however, the distribution density $E(t)$ defined by

$$E(t) = \mathrm{d}F(t)/\mathrm{d}t\,. \tag{5}$$

is more frequently used. In this case it will be expressed in the parametric form as

$$E(t) = E_t(r_t) = \frac{1}{Q} \cdot \frac{v(r_t)\,2\pi r_t}{[\mathrm{d}\vartheta(r_t)/\mathrm{d}r_t]}\,, \tag{6a}$$

which is a special form of the relationship (*15b*) from the first part of this analysis[1]. The expression (*6a*) can be rearranged using (*4b*) to give

$$E(t) = \frac{1}{Q} \cdot \frac{L^2\,2\pi r_t}{t^3(-\mathrm{d}v/\mathrm{d}r)|_{r=r_t}}\,, \tag{6b}$$

where apart from the parameter r_t also the residence time is included. It is customary to normalize[1] the distribution functions by introducing the normalized time variable Θ in the form of

$$\Theta = t/\bar{t} = tQ/V\,, \tag{7}$$

where the mean residence time $\bar{t}$ is

$$\bar{t} = \int_0^\infty E(t)\,t\,\mathrm{d}t = V/Q\,, \tag{8}$$

so that the normalized distribution density $E^+(\Theta)$ will be given by

$$E^+(\Theta) = \bar{t}E(\bar{t}\Theta)\,. \tag{9}$$

Further, the normalized velocity profile of a laminar tubular flow is obviously given by

$$w = v/U = v(\pi R^2/Q)\,, \quad y = r/R\,. \tag{10a, b}$$

Ultimately, the normalized residence time distribution function for a given velocity profile $w(y)$ can be written as

$$\Theta = \frac{1}{w(y_\Theta)}\,, \tag{11}$$

$$F^+(\Theta) = \int_0^{y_\Theta} w(y)\,2y\,\mathrm{d}y = w(y_\Theta)\,y_\Theta^2 + \int_0^{y_\Theta} (-\mathrm{d}w/\mathrm{d}y)\,y^2\,\mathrm{d}y; \tag{12}$$

and

$$E^+(\Theta) = \frac{2}{\Theta^3} \frac{y_\Theta}{(-\mathrm{d}w/\mathrm{d}y)|_{y=y_\Theta}} \tag{13}$$

and $y_\Theta = y_\Theta(\Theta)$ being for a given Θ the solution of the equation (*14*)

$$\Theta - 1/w(y_\Theta) = 0\,. \tag{14}$$

Non-Newtonian Tubular Flow

The kinematics of the non-Newtonian isothermal developed tubular flow is for a given tube-radius R and for a given volumetric flow rate Q (or alternatively for a given pressure drop $\Delta P/L$) fully determined by the viscosity function of the liquid concerned. Viscosity function will be usually expressed in terms of the apparent viscosity η,

$$\eta \equiv \tau/D \tag{15}$$

being the function of the shear stress

$$\eta = \eta[\tau]\,. \tag{16}$$

The radial shear stress distribution results from the solution of the momentum balance[6] in the form of

$$\tau = \tau_w y \tag{17}$$

where y is given by the equation (*10b*) and τ_w follows from the macroscopic momentum balance as

$$\tau_w = \frac{\Delta P}{L} \cdot \frac{R}{2}\,. \tag{18}$$

The expression for the local value of the velocity gradient will be obtained using equations (*15*)–(*18*) which after integration with the boundary condition $v(R) = 0$ leads to a radial profile of axial velocities

$$v(r) = (R/\tau_w) \int_{\tau_w(r/R)}^{\tau_w} (\tau/\eta[\tau])\, d\tau\,. \tag{19}$$

The volumetric flow rate expressed by means of the average velocity U will then be given by

$$U/R = (1/\tau_w^3) \int_0^{\tau_w} (\tau^3/\eta[\tau])\, d\tau\,, \tag{20}$$

where the use of equations (*3a*) and (*3b*) has been made. When expressions derived above are substituted into equations (*11*)–(*13*) and the normalized variables according to (*10a*) and (*10b*) applied, the normalized distribution functions will be obtained in a form including also dimensional parameters resulting from a dimensional material function $\eta(\tau)$. This formal drawback can be rectified, however, by using a normalized* viscosity function

$$m[s] = (1/\eta_1)\, \eta[s \cdot \tau_1]\,. \tag{21}$$

* The normalization of non-linear material functions has, apart from formal advantages, also further consequences leading finally to the concept of the rheological similarity[7–9].

in terms of dimensionless quantities

$$m \equiv \eta/\eta_1\,; \quad s \equiv \tau/\tau_1\,. \tag{22}$$

Using the variables defined above the solution of the problem of the developed velocity profile can be formulated as

$$A \equiv \tau_w/\tau_1\,, \quad B \equiv U\eta_1/R\tau_1 \qquad (23), (24)$$

$$B[A] \equiv (1/A^3)\int_0^A (s^3/m[s])\,\mathrm{d}s\,, \tag{25}$$

$$T = Ay\,, \quad (-\mathrm{d}w/\mathrm{d}y) = (1/B[A])\,(T/m[T])\,, \qquad (26), (27)$$

$$w(y) = (1/AB[A])\int_T^A (s/m[s])\,\mathrm{d}s\,, \tag{28}$$

$$w_{\max} = (1/AB[A])\int_0^A (s/m[s])\,\mathrm{d}s \tag{29}$$

and hence also the relationships for the distribution functions can be transformed into dimensionless forms

$$\frac{1}{\Theta} = w = \frac{1}{AB[A]}\int_{T_\Theta}^A \frac{s\,\mathrm{d}s}{m[s]}\,, \tag{30}$$

$$F^+(\Theta) = \begin{cases} 1 - \dfrac{1}{B[A]\,A^3}\displaystyle\int_{T_\Theta}^A \frac{(s^2 - T_\Theta^2)\,s\,\mathrm{d}s}{m[s]}\,; & \Theta \geqq \Theta_{\min} \\ 0 & ;\ \Theta < \Theta_{\min}\,. \end{cases} \tag{31}$$

$$E^+(\Theta) = \begin{cases} \dfrac{B[A]}{A}\,\dfrac{2}{\Theta^3}\,m[T_\Theta]\,; & \Theta \geqq \Theta_{\min} \\ 0 \quad ; & \Theta < \Theta_{\min}\,. \end{cases} \tag{32}$$

$$1/\Theta_{\min} = w_{\max}\,, \tag{33}$$

where T_Θ is a parameter the dependence of which upon Θ is implicitly given by equation *(30)*.

General Properties of Distribution Functions

The normalized laminar tubular velocity profile $w(y)$ satisfies the following normalisations

$$w(1) = 0\,, \quad (-\mathrm{d}w/\mathrm{d}y)|_{y=1} = 0\,, \tag{34, 35}$$

$$\int_0^1 w(y)\, 2y\, \mathrm{d}y = \int_0^1 (-\mathrm{d}w/\mathrm{d}y)\, y^2\, \mathrm{d}y = 1\,. \tag{36}$$

In addition to that, further conditions are valid for the isothermal flow

$$-\mathrm{d}w/\mathrm{d}y \geqq 0\,, \quad -\mathrm{d}^2w/\mathrm{d}y^2 \geqq 0\,, \tag{37, 38}$$

because viscosity functions of arbitrary liquid satisfy the conditions

$$m[s] \geqq 0\,, \quad \mathrm{d}(s/m[s])\mathrm{d}s \geqq 0\,. \tag{39, 40}$$

Consequently the variation of normalized distribution functions for different viscosity functions will be rather limited because they depend, according to equations (*12*)–(*14*), entirely upon the velocity profiles. Typical examples of velocity profiles and distribution functions are demonstrated in Figs 2–4 where "power-law" interpretation of viscosity function for $n = 0$, 1 and ∞ has been used[4].

Asymptotic Form of Distribution Functions for $\Theta \to \infty$

Near the wall, *i.e.* for $y \to 1$, the velocity of the liquid is very small, $w \to 0$ and $\Theta \to \infty$, compared with the average velocity in the tube. Under these conditions there will be similarly $T \to A$ or $m[T] \to m[A]$, and using equation (*32*) the following equation can be written for this limiting case

$$\frac{1}{2} \lim_{y_\Theta \to 1} (\Theta^3 E(\Theta)) = \frac{B[A]}{A}\,.\, m[A]\,. \tag{41}$$

Using equation (*27*) the previous equation can be rearranged into the form

$$E^+(\Theta) \approx \frac{1}{(-\mathrm{d}w/\mathrm{d}y)|_{y=1}}\,.\,\frac{2}{\Theta^3}\,; \quad \Theta \to \infty \tag{42a}$$

which transforms further into the expression

$$E^+(\Theta) \approx \frac{2n^*}{3n^* + 1}\,.\,\frac{1}{\Theta^3}\,; \quad \Theta \to \infty\,. \tag{42b}$$

for which the Metzner–Rabinowitsch equation

$$3 + \frac{1}{n^*} = (-\mathrm{d}w/\mathrm{d}y)|_{y=1}\,, \tag{43}$$

was used with the Metzner index n^* defined[10,11] as

$$n^* = \frac{\mathrm{d}\ln A}{\mathrm{d}\ln B} = \frac{\mathrm{d}\ln(R\Delta P/L)}{\mathrm{d}\ln(Q/R^3)}\,.$$

Using the definition equations for the distribution functions $F^+(\Theta)$ and $E^+(\Theta)$ their asymptotic form for $\Theta \to \infty$ will be

$$F(\Theta) \approx 1 - \frac{1}{(-\mathrm{d}w/\mathrm{d}y)|_{y=1}} \cdot \frac{1}{\Theta^2}\,, \tag{44a}$$

and

$$F^+(\Theta) \approx 1 - \frac{n^*}{3n^* + 1} \cdot \frac{1}{\Theta^2}\,. \tag{44b}$$

Limiting Form of Distribution Functions for $\Theta \to \Theta_{min}$

The velocity profile $w(y)$ reaches its maximum in the centerline of the tube, $w(0) = w_{max}$. Consequently, the portion of the liquid flowing with a velocity higher than w_{max} is nil and the minimum residence time will be $\Theta_{min} = 1/w_{max}$. For any time $\Theta \leqq \Theta_{min}$ there will be $F^+(\Theta) = 0$; $E^+(\Theta) = 0$. For a given viscosity function and given conditions of flow the value of the parameter Θ_{min} is determined by the equations (*29*) and (*33*). In general, only the limits can be found in which Θ_{min} can take place. From the condition $w_{max} > 1$ and from equation (*38*) it can be derived that $\Theta_{min} > 1/3$ if all other normalisation conditions are taken into account. For common non-Newtonian liquids for which the Metzner index is $0 < n^* < 1$ and the apparent viscosity is a non-rising function of the shear stress, *i.e.* $\mathrm{d}m[s]/\mathrm{d}s \leqq 0$ and $s \in \langle 0; A \rangle$, the following inequality is valid, $1/2 \leqq \Theta_{min} \leqq 1$.

Liquid fractions with residence times close to the minimum value Θ_{min} will not be too far from the centre line of the tube where the velocity profile is relatively flat so that it can be approximated by a piston-type profile. It follows from this approximation that $E^+(\Theta)$ rises relatively steeply for values of Θ near to Θ_{min} and after reaching a maximum its decrease is again relatively fast in accordance with the character of the impulse function. This will also be apparent from the $E^+(\Theta)$ curves given in Fig. 3. For the line that corresponds with the position $y = 1$ (except for viscoplastic liquids), the function $E^+(\Theta)$ is given by an indefinite expression 0/0. As long as this can be evaluated at all, equation (*45*) will be used for that purpose

$$\lim_{\Theta \to \Theta_{min}} E^+(\Theta) = \frac{2B[A]}{A\Theta_{min}^3} m[0] \tag{45}$$

based upon the expression (32). The limit form of the function $E^+(\Theta)$ for the case $(\Theta - \Theta_{min}) \to 0_+$ depends upon the limit form of the function $m[s]$ for $s \to 0$. Therefore the limit behaviour of distribution functions cannot be studied without making assumptions about the character of viscosity function. This will become equally obvious from the first derivative of the function $E^+(\Theta)$ which can be written in the form

$$\frac{dE^+}{d\Theta} = -\frac{E^+(\Theta)}{\Theta} \cdot \left[\left(3 + \frac{w(y_\Theta)}{w'(y_\Theta)}\right)\left(\frac{1}{y_\Theta} - \frac{w''(y_\Theta)}{w'(y_\Theta)}\right)\right] \tag{46a}$$

or in the form

$$\frac{dE^+}{d\Theta} = -\frac{E^+(\Theta)}{\Theta}\left(3 - \frac{2AB}{\Theta} \frac{dm[s]}{ds^2}\bigg|_{s=\Upsilon_\Theta}\right), \tag{46b}$$

Liquids with Finite Zero-Shear Viscosity

The viscosity function can be expanded for slow shear rates into a satisfactorily converging even power series with a non-zero constant term[12]. By a suitable choice

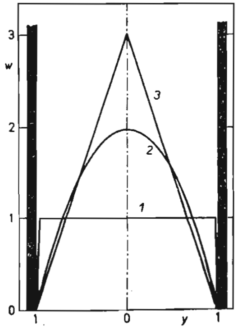

FIG. 2

Velocity Profiles of the Tubular Power-Law Flow

1 $n = 0$; *2* $n = 1$; *3* $n = \infty$.

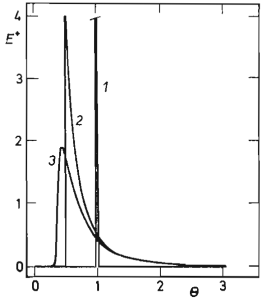

FIG. 3

Normalized Distribution Densities of Residence Times

Key as for Fig. 2.

of the normalisation factors τ_l and D_l the normalized form of this expansion can be written as

$$m[s] = 1 + \alpha_2 s^2 + \alpha_4 s^4 + \dots \tag{47}$$

and using the relationships (45) and (47) the linearized limit form of $E^+(\Theta)$ can be given as

$$E^+(\Theta) = \frac{2B}{A\Theta_{\min}^3}\left[1 - \left(3 - \frac{2AB\,\alpha_2}{\Theta_{\min}}\right)\frac{\Theta - \Theta_{\min}}{\Theta_{\min}}\right]. \tag{48}$$

It is possible to derive also a non-linear asymptotic expression valid in a wider range of Θ, the validity of which is limited only by the conditions $\alpha_2 s^2 \gg \alpha_2 s^4$ and by the requirement of a sufficient convergence of the series (47). In the expression (49)

$$\frac{1}{\Theta_{\min}} - \frac{1}{\Theta} = \frac{1}{AB}\int_0^{T_\Theta} \frac{s\,\mathrm{d}s}{m[s]}. \tag{49}$$

derived from equations (26), (29), (30) and (33) the term $s/m[s]$ can be expanded and after neglecting the terms of the fourth and higher orders and inverting the result for an explicit $\Theta = \Theta[T_\Theta]$ the limit form of the viscosity function can be obtained. Substituting it then into the expression (32) the asymptotic form (50) will be found

$$E^+(\Theta) = (2B/A)\,\{2 - [1 - 4\alpha_2(AB/\Theta_{\min})\,(1 - \Theta_{\min}/\Theta)]^{1/2}\}/\Theta^3, \tag{50}$$

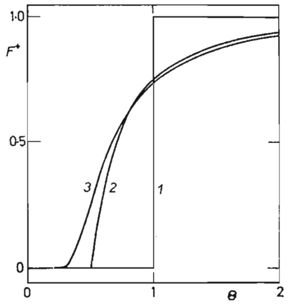

FIG. 4

Normalized Residence Time Distribution Key as for Fig. 2.

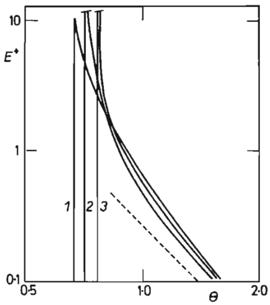

FIG. 5

Normalized Distribution Densities in Logarithmic Coordinates, $n^* = 0{\cdot}25$

1 Eyring Model, *2* power-law, *3* Bingham model.

in which the initial non-linear character of the viscosity function is expressed by the parameter α_2. When $\Theta \to \Theta_{min}$, equation (*50*) goes over into a linear form (*48*).

It is therefore possible to determine the limit form of the function $F^+(\Theta)$ if the function $E^+(\Theta)$ is known. So it will be for the linearized form of $E^+(\Theta)$

$$F^+(\Theta) \approx E(\Theta_{min}) \cdot (\Theta - \Theta_{min}) + \left.\frac{dE^+(\Theta)}{d\Theta}\right|_{\Theta=\Theta_{min}} \cdot \frac{(\Theta - \Theta_{min})^2}{2}, \qquad (51)$$

where the values of parameters follow from equation (*48*). To the best of the authors'-knowledge, all experimentally obtained viscosity functions satisfy the condition $(dm/ds) \leqq 0$, *i.e.* $\alpha_2 \leq 0$ as long as a finite zero-shear viscosity exists. It follows from equation (*48*) or (*50*) that in such a case $E^+(\Theta)$ is a descending function for all $\Theta > \Theta_{min}$ the shape of which is comparable with the curve 2 in Fig. 3.

For the sake of completeness, the case of $\alpha_2 > 0$ should also be investigated. It is obvious from the generally valid relationship (*46b*) that for sufficiently large values of Θ the function $E^+(\Theta)$ is always a descending one. If, however, α_2 satisfied the condition $3 - (2AB/\Theta_{min})\,\alpha_2 \leqq 0$ then there is $(dE^+/d\Theta) \leqq 0$ for $\Theta = \Theta_{min}$ and the function $E^+(\Theta)$ will have a minimum at the point $\Theta_0 = (2AB/3)_2$.

It is possible to get a qualitative picture about the values of α_2 such as to enable the existence of an untypical $E^+(\Theta)$ function when assuming that a formula $m(s) = 1 + \alpha_2 s^2$ satisfactorily describes the viscosity function in the entire region of $s \in \langle 0; A \rangle$. It follows from expressions (*29*) and (*33*) that

$$(2\alpha_2 AB)/\Theta_{min} = \ln(1 + \alpha_2 \cdot A^2)\,.$$

If, therefore, α_2 satisfies the condition $\alpha_2 A^2 > e^3 - 1$ a round maximum can be detected on the $E^+(\Theta)$ curve approximately in the point corresponding with $\Theta_0 = \ln(1 + \alpha_2 A^2)/3$. If, however, the value of $\alpha_2 A^2$ will be within the limits $(0; e^3 - 1)$, no round extreme can be found. Instead of it, as a more detailed analysis indicates, there will be an inflexion point. Finally, the $E^+(\Theta)$ will be convex for the whole region $\Theta > \Theta_{min}$ if α_2 satisfies the condition $\alpha_2 A^2 < 0$.

Liquids with a Power-Law Viscosity Function

In general, the limit viscosity function cannot be always expressed in terms of an even power series (*47*) because the possibility cannot be excluded that there will be either $\lim_{s \to 0} m[s] = \infty$ or

$$\begin{cases} \lim_{s\to 0} m[s] \cdot s^{k+1} = 0 \\ \lim_{s\to 0} m[s] \cdot s^k = 1 \end{cases},$$

where k is an arbitrary integer. These cases can be studied using a generalized power expansion

$$m[s] = s^{(1-1/n)} \cdot (1 + \beta_1 s + \beta_2 s^2 + \ldots) \qquad (52)$$

where n is a real positive number and $\beta_1 \neq 0$. No sensible information can be obtained, however, about the limit character of the function $E^+(\Theta)$ in the linearized form (*48*) because, according to equation (*52*), the values of the function $m[s]$ and their derivatives are either infinite or zero for all $n \neq 1$. It is possible, however, to use a procedure starting by substituting equation (*52*) into equation (*49*) and by expanding the result into a series for $\Theta \to \Theta_{min}$ and $T_\Theta \to 0$. In this way an expression for the explicit residence time function will be obtained, the inversion of which will lead to

$$T_\Theta = Z^{n/(n+1)} \cdot \left(1 + \frac{\beta_1 n}{1 + 2n} \cdot Z^{n/(n+1)} + \ldots\right) \qquad (53)$$

where

$$Z = \left(\frac{1}{\Theta_{min}} - \frac{1}{\Theta}\right) AB \frac{n}{1 + n} \,. \qquad (54)$$

The series (*53*) converges satisfactorily for $\Theta \to \Theta_{min}$ so that the corresponding expression for $E^+(\Theta)$ will result as

$$E^+(\Theta) = \frac{2B}{A\Theta^3} \cdot Z^{(1-n)/(1+n)} \cdot \left(1 + \frac{\beta\, 3n}{1 + 2n} \cdot Z^{n/(n+1)} + \ldots\right). \qquad (55)$$

By analysing equation (*55*) it follows that for $n < 1$ there is $\lim_{\Theta \to \Theta_{min}} E^+(\Theta) = \infty$ and $\lim_{\Theta \to \Theta_{min}} (\mathrm{d}E^+/\mathrm{d}\Theta) = -\infty$. On the other hand for $n > 1$ there is $E^+(\Theta_{min}) = 0$ and $(\mathrm{d}E^+/\mathrm{d}\Theta)|_{\Theta=\Theta_{min}} = 0$. In this case a round maximum must exist on the $E^+(\Theta)$ curve the position Θ_0 of which will be approximately given (provided $T_{\Theta_0} \ll 1$) by the relationship*

$$\frac{\Theta_0}{\Theta_{min}} = 1 + \frac{n - 1}{3(n + 1)} \,. \qquad (56)$$

Viscoplastic Liquids

For viscoplastic liquids the yield stress τ_0 is a characteristic parameter. The shear rate under viscometric flow conditions reaches a zero value if the stress

* This is in contradiction with the shape of the $E^+(\Theta)$ curve for $n = 1{\cdot}4$ in Fig. 1 of the paper by Novosad and Ulbrecht[4]. In fact their curve should be as the curve 3, Fig. 3 of this work.

in the flowing liquid falls below the limit τ_0. For a suitably chosen normalizing parameter $\tau_I = \tau_0$ the limit course of viscosity function can be expressed as

$$1/m[s] = 0\,, \quad \text{for} \quad s \in \langle 0\,;1\rangle\,. \tag{57}$$

It follows from equation (27) that the velocity gradient is zero within the limiting $y \in \langle 0; 1/A\rangle$ and thus $w = w_{max}$ and $\Theta = \Theta_{min}$. In this region no information can be obtained about the function $E^+(\Theta)$ from equations (32) or (13) since the statement $E^+(\Theta_{min}) = \infty$ has only qualitative meaning.

For a quantitative analysis of distribution functions, however, some results from the first part of this work[1] can be used. For this particular purpose the region of the flowing liquid will be divided into two coaxial parts: the piston-flow region near the centre line of the tube where $0 \leqq y \leqq 1/A$ and $\Theta = \Theta_{min}$ and the region of the shear flow for which there is $1/A < y \leqq 1$ and $\Theta > \Theta_{min}$. The normalized distribution density for the piston-flow region $E_p^+(\Theta)$ can be expressed by means of the impulse function $\delta(x)$ as

$$E_p^+(\Theta) = \delta(\Theta - \Theta_{min})\,. \tag{58}$$

Using the rules for the superposition of normalized functions $E^+(\Theta)$ for a set of parallel-arranged flow systems[1] the distribution density for the system as a whole can be written as

$$E^+(\Theta) = \varepsilon_p \delta(\Theta - \Theta_{min}) + E^+(\Theta)\,, \tag{59}$$

where

$$\varepsilon_p = \frac{\int_0^{1/A} w(y)\, 2y\, dy}{\int_0^A w(y)\, 2y\, dy} = \frac{1}{\Theta_{min} A^2} \tag{60}$$

and where the function $E_s^+(\Theta)$ has been defined for $\Theta \geqq \Theta_{min}$ by the relationships (13) or (32).

Hence the function $E^+(\Theta)$ for the flow of viscoplastic fluids will be*

$$E^+(\Theta) = \begin{cases} 0 & \Theta < \Theta_{min} \\ \dfrac{\delta(\Theta - \Theta_{min})}{\Theta_{min} A^2} + \dfrac{2B}{A\Theta^3}\, m[T_\Theta]\,; & \Theta \geqq \Theta_{min}\,. \end{cases} \tag{61}$$

The function $F^+(\Theta)$ can be calculated in this case also from expressions (12) or (31) bearing in mind that the following inequalities are valid

$$\lim_{\Theta \to \Theta_{min}} F^+(\Theta) = 1 - \frac{1}{BA^3} \int_1^A \frac{(s^2 - 1)\, s\, ds}{m[s]} = \frac{1}{\Theta_{min} A^2}\,. \tag{62}$$

* The character of the function $E_s^+(\Theta)$ for $\Theta \to \Theta_{min}$ can be investigatied using methods given in the two previous paragraphs. On the other hand, however, the behaviour of $m[s]$ and its first derivative can be studied at $s \to 1_+$ instead of at $s \to 0_+$ and the expansion must be done at $(s - 1)$ instead of at s.

NON-NEWTONIAN RHEOLOGICAL MODELS

So far only the general expression for the viscosity function $m[s]$ has been used which is an approach most suitable for this sort of problem. In order to understand the variability of distribution functions for various types of viscosity function the use of empirical formulae known as non-Newtonian rheological models will be made.

Examples of the most common models are given in Table I. For those, the normalisation of the equations describing various aspects of the tubular flow is possible applying methods discussed above. Further, the expressions for B, w_{max}, $w(y)$, and n^* for selected non-Newtonian models are given in Tables II. For all those the relationships of the type $\Theta(T) = 1 - \Theta_{min}/\Theta$ can be inverted into the form $T = \Phi^{-1}(1 - \Theta_{min}/\Theta)$ using algebraic or other tabulated functions. Because the functions $E^+(T_\Theta)$ and $F^+(T_\Theta)$ for these models can be expressed in an equally simple fashion, the distribution functions $E^+(\Theta)$ and $F^+(\Theta)$ will result in an explicit form. The resulting distribution functions for a number of rheological models are given in Figs 5—10 for identical values of the Metzner index n^* and thus also for identical values of the normalized velocity gradient of the wall. Therefore the distribution functions given in any one figure have common asymptotic solution depicted by dotted lines.

RESULTS AND THEIR DISCUSSION

For a fully developed laminar flow under the given macroscopic parameters of the flow* and within variable physico-chemical properties the velocity profile and thus

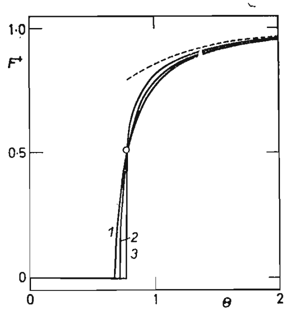

FIG. 6

Normalized Distribution Functions in Linear Coordinates, $n^* = 0{\cdot}25$

Key as for Fig. 5.

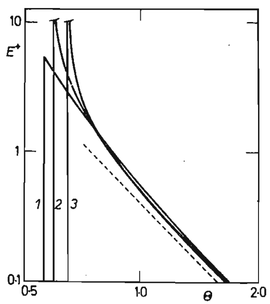

FIG. 7

Normalized Distribution Densities, $n^* = 0{\cdot}5$

Key as for Fig. 5.

* The laminar velocity profile for a given liquid is entirely determined by fixing just one from the following pairs of process variables: $(R, \Delta P/L)$; (R, Q); $(Q, \Delta P/L)$.

the distribution functions are entirely determined by the viscosity function. It has been found that the distribution function can be approximated by its asymptotic course, equations (*42b*) and (*44b*), with an accuracy better than 10% for that part of flow

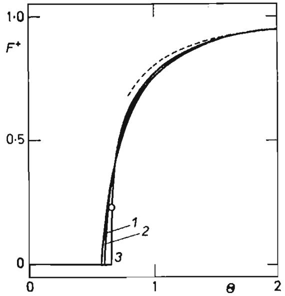

FIG. 8

Normalized Distribution Densities, $n^* = 0{\cdot}5$

Key as for Fig. 5.

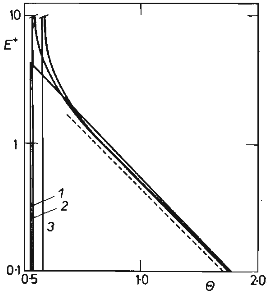

FIG. 9

Normalized Distribution Functions, $n^* = 0{\cdot}75$

Key as for Fig. 5.

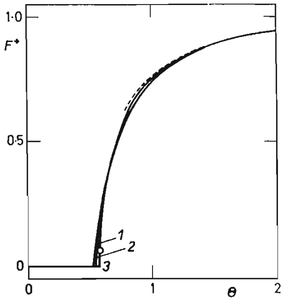

FIG. 10

Normalized Distribution Functions, $n^* = 0{\cdot}75$

Key as for Fig. 5.

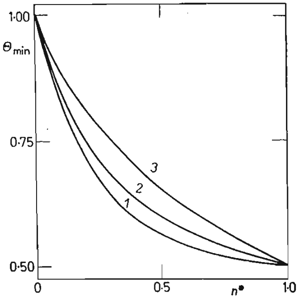

FIG. 11

Dependence of Θ_{min} upon n^* for Selected non-Newtonian Models

1 Eyring model, *2* power-law, *3* Bingham model.

TABLE I
Some More Common Non-Newtonian Models and Their Normalization

Non-Newtonian model	Transformation equation	Normalized form of the non-Newtonian model
Power		
$\tau = KD^n$	$\eta_I^n \tau_I^{1-n} = K$	$1/m = s^{1/n-1}$
Eyring		
$D = D_I \sinh(\tau/\tau_I)$	—	$1/m = \sinh(s)/s$
Bingham		
$\tau = \tau_0 + \mu_B D$	$\eta_I = \mu_B$ $\tau_I = \tau_0$	$1/m = (s - 1)/s$
Rabinowitsch		
$D = a \cdot \tau + b\tau^3$	$\eta_I = a$ $\eta_I/\tau_I = b$	$1/m = 1 + s^2$
Bulkley-Herschel		
$\tau = \tau_0 + KD^n$	$\tau_I = \tau_0$ $\eta_I^n \tau_I^{1-n} = K$	$1/m = (s - 1)^{1/m}/s$
Ree-Eyring		
$\tau = aD + b \operatorname{arsinh}(D/D_I)$	$\tau_I = aD_I + b$ $E = b/\tau_I$ $p = D/D_I = s/m$	$m = m[p] = (1 - E) + E \operatorname{arsinh}(p)/p$

where the residence time is larger than the average one, *i.e.* for $\Theta > 1$. In this context it is essential to remember that for asymptotic solutions the viscosity function is fully described by the Metzner index n^*.

In order to test the deflections of distribution functions for different viscosity functions various cases have been compared being characterized by the same value of n^*, *i.e.* having the same asymptotic solution. For that purpose the functions $E^+(\Theta)$ and $F^+(\Theta)$ calculated for a power-law liquid with $n = n^*$ have been used. In principle, there are two reasons for doing that: *1.* Only for the power-law behaviour a simple and unambiguous relationship between the macroscopic parameter n^* and a material parameter n exists which does not depend upon the flow variables as long as the flow is laminar. *2.* The concept of the Metzner

TABLE II

Fundamental Normalized Relationships Describing the Non-Newtonian Tubular Flow for Selected Non-Newtonian Models

Model	$B[A]$	$w_{max} = 1/\Theta_{min}$	$\Phi(T) = 1 - \frac{w(y)}{w_{max}} = 1 - \frac{\Theta_{min}}{\Theta}$	$n^*(A)$
Power	$\frac{n}{3n+1} \cdot A^{1/n}$	$\frac{1+3n}{1+n}$	$(T/A)^{1/n+1}$	n
Eyring[a]	$\frac{1}{A}\left\{ch - \frac{2}{A}\left[sh - \frac{1}{A}(ch - 1)\right]\right\}$	$\frac{ch - 1}{AB[A]}$	$\frac{\cosh(T) - 1}{\cosh(A) - 1}$ [b]	$\left(\frac{\sinh(A)}{B(A)} - 3\right)^{-1}$
Bingham	$\frac{(A-1)^2}{A^3} \cdot \frac{3A^2 + 2A + 1}{12}$	$\frac{6A^2}{3A^2 + 2A + 1}$	$\left(\frac{T-1}{A-1}\right)^2$	$\frac{(A-1)^2(3A^2 + 2A + 1)}{3(A^4 - 1)}$
Rabinowitsch	$\frac{A}{4} + \frac{A^3}{6}$	$\frac{6 + 3A^2}{3 + 2A^2}$	$\frac{2T^2 + T^4}{2A^2 + A^4}$	$1 - \frac{2}{3} \cdot \frac{A^2}{A^2 + 1/2}$
Bulkley-Herschel	$\frac{(A-1)^{1/n+1}}{A^3} \cdot M(A, n)$	$\frac{A^2}{(1/n + 1)\, M(A, n)}$	$\left(\frac{T-1}{A-1}\right)^{1/n+1}$	$\frac{(A-1)\, M(A, n)}{A^3 - 3(A-1)\, M(A, n)}$
	$M(A, n) = \frac{(A-1)^2}{1/n + 3} + \frac{2(A-1)}{1/n + 2} + \frac{1}{1/n + 1}$			

[a] sh = sinh (A), ch = cosh (A); [b] Expressions for $B(A)$ and for $M(A, n)$ are in the first column.

TABLE III

Normalized Distribution Densities of Residence Times and Normalized Residence Time Distribution for Selected Non-Newtonian Models

Model	$E^+(\Theta)$
Power	$2n/(3n+1) \,.\, 1/\Theta^3 \,.\, (1 - 1/\Theta^*)^{-(1-n)/(1+n)}$
Eyring	$2B(A)/A\Theta^3 \,.\, T_\Theta/\sinh T_\Theta$, $T_\Theta = \operatorname{arcosh}[1 + (\cosh A - 1)(1 - 1/\Theta^*)]$
Bingham	$\delta(\Theta - \Theta_{min})/\Theta_{min}A^2 + (A-1)/A^4 \,.\, (3A^2 + 2A + 1/6\Theta^3) \,.$ $.\, (A - 1 + (1/[(1 - 1/\Theta^*)^{1/2}]))$
Rabinowitsch	$1/6\Theta^3 \,.\, (3 + 2A^2)/[1 + (2A^2 + A^4)(1 - 1/\Theta)]^{1/2})$
Bulkley-Herschel[a]	$[\delta(\Theta - \Theta_{min})/\Theta_{min}A^2] + [(A-1)/A^4] \,.\, M(A, n) \,.\, 2/\Theta^3 \,.$ $.\, [1 + (A-1)(1 - 1/\Theta^*)^{n/(n+1)}]/[(1 - 1/\Theta^*)^{1/(n+1)}]$

[a] Expression for $M(A, n)$ see Table II; [b] the shape of function $T_\Theta = T(\Theta)$ for the Eyring model see the first column. [c] For the function $M = M(A, n)$ for the Bulkley-Herschel model see Table II.

index n^* proved itself to be an extremely useful tool for dealing with transport processes in tubular flows[7-10]. Apart from that the power-law represents a sort of "middle-of-the-road" interpretation between the Bingham and Eyring models.

Using the relationships given in Tables I–III the viscosity function have been calculated for the power-law, Bingham and Eyring models and the distribution functions were compared for the values $n^* = 0{\cdot}05, 0{\cdot}10 \ldots 0{\cdot}90, 0{\cdot}95$. It has been found that the functions $E^+(\Theta)$ and $F^+(\Theta)$ calculated for the Eyring and Bingham model in the region $\Theta > 1$ do not differ by more than 2·5% from the results for the power-law model. Some results for the $n^* = 0{\cdot}25$, 0·50 and 0·75 are illustrated in Figs 5–10.

For the region $\Theta < 1$ the deflections for different models grow larger and for Θ_{min} the approximation has only a qualitative character. A comparison will show that for $n^* = 0{\cdot}25$ and $\Theta = 0{\cdot}76$ the distribution function calculated for the power-law and Eyring models will be $F^+(0{\cdot}76) = 0{\cdot}45$ whilst for the Bingham model it is $F^+(0{\cdot}76) = 0$. This is because the limit distribution function strongly depends upon the limit viscosity function and further because the value of the parameter Θ_{min} depends to a certain extent upon the viscosity function as well even for fixed n^*. For a given

TABLE III
(*Continued*)

$F^{+}(\Theta)$	
$(1 - 1/\Theta^*)\,[2n/(n+1)]\,(1 + 2n/(n+1)\,.\,1/\Theta^*)$	(71a)
$[T_{\Theta}^2 \cosh(A) + 2\cosh(T_{\Theta}) - 2T_{\Theta}\sinh(T_{\Theta}) - 2]/A^3B[A]$	(71b)
$[6 + 3(A-1)^2\,.\,(1 - 1/\Theta^{*2}) + 4(2 + 1/\Theta^*)(A-1)(1 - 1/\Theta^*)^{1/2}]/(3A^2 + 2A + 1)$	(71c)
$[2 + (A^4 + 2A^2)(1 + 2/\Theta^*)]\,\{([1 - (A^4 + 2A^2)\,.\,(1 - 1/\Theta^*)]^{1/2} - 1)/(2A^6 + 3A^4)\}$	(71d)
$1 - \frac{(A-1)}{M(A,n)}\,.\left\{\frac{1/\Theta^*\,.\,(1 - 1/\Theta)^{n/(2+n)}\,[2 + (1 + 1/\Theta^*)^{n/(2+n)}\,.\,(A-1)]}{1/n + 1} + \frac{2[1 - (1 - 1/\Theta^*)^{(1+2n)/(1+n)}]}{1/n + 2} + \frac{A-1}{1/n+3}\,.\,[1 - (1 - 1/\Theta^*)^{(1+3n)/(1+n)}]\right\}.$	(71e)

type of viscosity function the limit properties of distribution functions can be characterized by the forms of these functions in terms of $(1 - \Theta_{min}/\Theta)$. Potential deflections of Θ_{min} for a given n^* are apparent from Fig. 11 and they correspond with the overall range of variability of viscosity function.

Any further discussion of these discrepancies and their interpretation in terms of distribution functions seems to have, however, only a limited value. Mainly two reasons speak for that: *1.* The limit visocity function $m[s]$ for $\tau \to 0$ (or $s \to 0$) are experimentally difficult to obtain* and the extrapolation procedure depends upon the interpolation formula used. *2.* Rather than the distribution function itself its q-th moment is more frequently used in actual applications. Unfortunately, this cannot be used if the liquid fully adheres to the wall, because then $\nu_q = \infty$ for $q \geqq 2$.

So far the most frequent application of distribution function is the prediction of conversion functions in continuous flow-reactors. In this case some rather common types of homogeneous irreversible reaction equations can be chosen for the integral

* For most experimental arrangements the range of measured shear stresses does not exceed two orders of magnitude and any measurement in the region of shear rates smaller than $10^{-1}\,s^{-1}$ and larger than $10^4\,s^{-1}$ requires specially designed instruments suitable usually only for certain types of liquids (*e.g.* dilute polymer solutions).

characteristics as an alternative. A systematic testing of deflections of $E^+(\Theta)$ for various rheological models at the same n^* would probably prove that these deflections are insignificant. This conclusion can also be substantiated by considering the expression of the conversion of an irreversible second-order reaction[4]

$$X(q) = \int_{\Theta_{\min}}^{\infty} \frac{1}{q \cdot \Theta + 1} \, E^+(\Theta) \, . \, d\Theta \qquad (63)$$

which undergoes only a ten per cent change of its value when the conditions of flow change from the Newtonian ($n^* = 1$) to the piston-type flow ($n^* = 0$). This is true even in the region where the conversion reaches about 50 per cent. In fact, this example represents the largest possible change provided that only the shear-thinning liquids are being concerned.

There is one more reason for neglecting the deviations of $E^+(\Theta)$ at n^* = idem even for $\Theta < 1$. This is the fact that for $\Theta \geqq 1$ not only the function $E^+(\Theta)$ but also the function $F^+(\Theta)$ is fairly invariable for different rheological models. It follows therefore that for a given n^* always approximately the same proportion of the liquid has its resistance time Θ larger than one so that the differences in distribution functions are mainly concentrated in the interval $\Theta \in \langle \Theta_{\min}, 1 \rangle$.

The extent of reaction conditions under which the differences of distribution functions for a given n^* can significantly influence the overall chemical conversion is still uncertain.

The authors are indebted to Dr K. Wichterle and Dr P. Mitschka for incentive discussions and to Miss S. Nováková for her assistance in numerical and computational calculations.

LIST OF SYMBOLS

A	normalized pressure loss, Eq. (*23*)
B	normalized velocity grandient, Eq. (*24*)
D	rate of deformation (s^{-1})
D_I	material parameter of viscosity function (s^{-1})
$E(t)$	distribution density of residence time, (s^{-1})
$E^+(\Theta)$	normalized distribution density
$F(t)$	residence time distribution function, dimensionless
$F^+(\Theta)$	residence time distribution function for a normalized argument, dimensionless
K	consistency coefficient, parameter of the power-law viscosity function, *Eq.* (*1*), $(g\ cm\ s^{n-2})$
L	the length of a finite section of the tube, (cm)
$m[s]$	normalized form of the viscosity function, Eq. (*22*)
n	dimensionless parameter of the power-law viscosity function, Eq. (*1*)
n	dimensionless parameter, Eq. (*52*)
n^*	dimensionless Metzner index (apparent flow index), Eq. (*41*)
$p \equiv s/m$	normalized shear rate
ΔP	pressure loss along the tube section L $(g\ cm^{-1}\ s^{-2})$
Q_t	volumetric flow rate for a liquid portion with a residence time shorter than t $(cm^3\ s^{-1})$
Q	total volumetric flow rate $(cm^3\ s^{-1})$
r	radial coordinate (cm)

r_t	radius, Eq. (*30*) (cm)
R	radius of a tube (cm)
s	normalized shear stress in the expressions for the normalized viscosity function
T	normalized shear stress for tubular flow, Eq. (*26*)
T_Θ	normalized shear stress for a given value of Θ, Eq. (*30*)
t	time variable (s)
$\bar{t}$	mean residence time, Eq. (*8*) (s)
U	mean velocity (cm s^{-1})
V	volume of the continuous flow system (cm^3)
w	normalized velocity, Eq. (*10a*)
w_{max}	normalized maximum velocity
y	normalized radial coordinate
y_Θ	normalized radial coordinate for a given value of Θ
z	axial coordinate (cm)
α_2, α_4	parameters of limit viscosity function
β_1	parameter of the limit viscosity function
$\delta(x)$	normalized impulse (Dirac) function
ε_p	fraction of the liquid which flows at the maximum velocity under viscoplastic flow
η	non-Newtonian apparent viscosity $(\text{g cm}^{-1}\,\text{s}^{-1})$
η_I	material parameters of viscosity function $(\text{g cm}^{-1}\,\text{s}^{-1})$
ϑ	transit time along a given streamline (s)
Θ	normalized residence time, Eq. (*7*), (*11*)
Θ_{min}	minimal value of the normalized residence time
Θ_0	value of Θ for which $E^+(\Theta)$ gets a continuous maximum
$\Theta^* \equiv \Theta/\Theta_{min}$	
μ_B	parameter of the Bingham model of the viscosity function $(\text{g cm}^{-1}\,\text{s}^{-1})$
ν_q	integral moments of distribution functions, Eq. (*63*)
φ	angular variable
τ	shear strees $(\text{g cm}^{-1}\,\text{s}^{-2})$
τ_I	material parameter of the viscosity function $(\text{g cm}^{-1}\,\text{s}^{-2})$
τ_0	yield stress $(\text{g cm}^{-1}\,\text{s}^{-2})$
τ_w	wall shear stress $(\text{g cm}^{-1}\,\text{s}^{-2})$
τ_{rz}	rz-component of the shear stress tensor in cylindrical coordinates (r, φ, z)

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