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FLOW CURVE DETERMINATION FOR NON-NEWTONIAN FLUIDS

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THIS REPORT DESCRIBES a student laboratory experiment for the determination of the flow curve of a non-Newtonian fluid using a capillary viscometer with continuously varying pressure head. The experiment exposes the student to the concepts of non-Newtonian flow analysis, as well as non-linear parameter estimation techniques. Computer aided data analysis is included as part of the experiment.

APPARATUS AND PROCEDURE

The viscometer is shown schematically in Fig. 1. It is a modification of one described some years ago by Cerny [1]. The instrument consists primarily of a precision bore capillary A and a 50 c.c. buret B. The capillary A is placed horizontally with one end inserted into a rubber stopper which is sealed to the collecting flask F and the other end connected to the buret B by means of a piece of tygon tubing. The pinch clamp C is a convenience for filling the viscometer. The flask F has a side-arm which is extended with a piece of tubing to the atmosphere. The buret B is jacketed by a 2-inch diameter glass tube. The water bath is kept at a desired temperature by a regulator G. The regulator unit contains a pump which is used for circulation of water through the jacket. This arrangement assures constant temperature for the measurements.

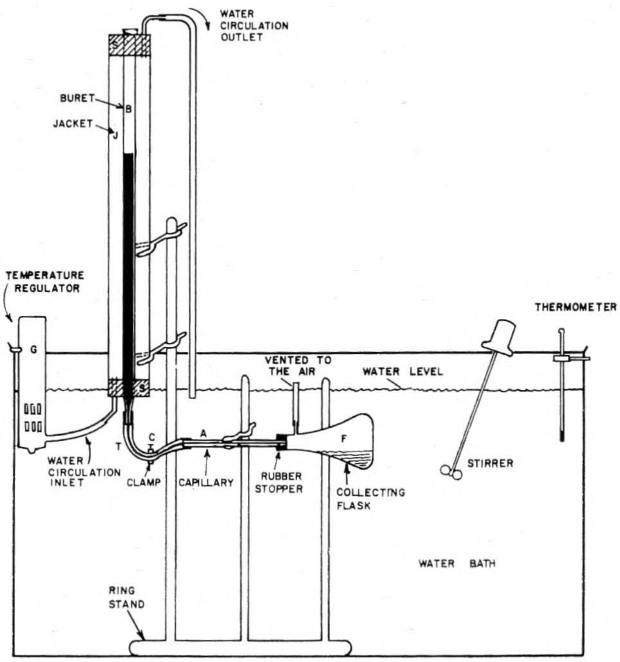
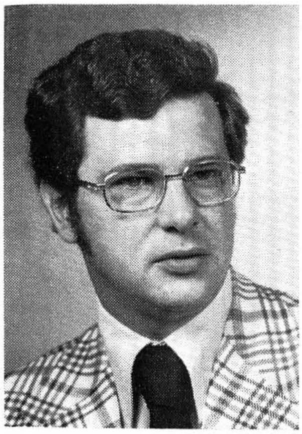


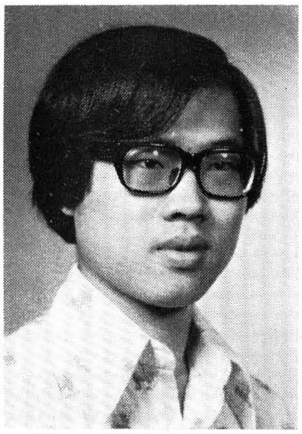
Fig. 1. Schematic diagram of the apparatus.

In operation, the buret, connecting tubing and capillary are filled with the test fluid and the clamp C put in place. Care should be taken to avoid trapping bubbles in the line. Generally the buret is filled well above the top graduation. If the test fluid is not at the bath temperature, about 10 minutes should be allowed to bring it up to bath temperature before starting a run. A run is started by opening clamp C, permitting the fluid in the buret to flow through the capillary. A stopwatch with a split hand feature is used to time the descent of the meniscus in the buret at selected graduations (i.e. 0, 5, 10, 15, . . .). The times corresponding to the selected graduations are recorded. Readings can be taken until the meniscus passes the last graduation on the buret or until the descent of the meniscus is too slow to be measurable. A minimum of three sets of graduation (x) versus time data are taken for a given sample. An average of the three sets is used for data analysis.

SUPPORTING DATA

THE LENGTH OF THE capillary is measured directly. The capillary radius is determined by filling it with mercury, weighing the thread of mercury, and calculating the radius from the





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volume of the thread. The volume is given by V = (mass of Hg) ÷ (density of Hg at measurement temperature). The radius then follows from $R = (V/\pi L)^{1/2}$. A minimum of three determinations are recommended.

The buret cross section is determined by measuring the distance between terminal graduations (i.e. h_o - h_{50}) and dividing the buret volume by this result.

$$A = 50/(h_0 - h_{50})$$

A relation between the buret graduations and the height of the meniscus relative to the capillary outlet is also required for data analysis. Noting the buret graduation as x and the measured distance between the last buret graduation and the capillary outlet as (h_{50} - h_c), the following expression can be written

$$h = \frac{50 - x}{A} + (h_{50} - h_c) \tag{1}$$

This gives the height of the meniscus relative to the capillary as a function of the buret graduation reading x.

The test fluid density, if unknown, is determined at the bath temperature with the aid of a pycnometer.

THEORETICAL

THE FLOW SITUATION of the present viscometer is very similar to that of a problem presented by Bird et al. [2]. Hence a quasi steady-state approach is used for the theoretical analysis. The theoretical development for Newtonian flow in this viscometer has been discussed by Cerny [1] and is outlined below. This will be followed by the analysis for non-Newtonian flow. The flow of a Newtonian fluid in a capillary tube is described by the Poiseuille, equation,

$$\Delta P = \frac{8\eta LQ}{\pi R^4} \tag{2}$$

This expression relates the pressure drop ΔP across the capillary (of radius R and length L) to the volume rate of flow Q and the coefficient of viscosity η. For the viscometer the pressure drop at any moment is also given by

$$\Delta P = \rho g h \tag{3}$$

where h is the height of liquid column in the buret relative to the capillary, ρ the fluid density and g the acceleration of gravity. The volume rate of flow at any moment can be expressed as

$$Q = -A\frac{dh}{dt} \tag{4}$$

where A is the cross sectional area of the buret.

The experiment exposes the student to the concepts of non-Newtonian flow analysis as well as non-linear parameter estimation techniques. Computer aided data analysis is included as part of the experiment.

The combination of equations (2), (3) and (4), followed by integration results in an expression relating h and t

$$\ln h = -\frac{\pi R^4 \rho g}{8LA\eta} t + C = -\frac{B\rho}{\eta} t + C = mt + C \tag{5}$$

where

$$B = \frac{\pi R^4 g}{8LA} \quad \text{and} \quad m = \frac{-B\rho}{\eta}$$

Thus a plot of $\log_{10}h$ versus t should be linear. The viscosity of a Newtonian fluid can be evaluated from the slope (m) provided that the instrumental dimensions and the fluid density are known.

In the case of a non-Newtonian fluid, the "viscosity" is not constant and varies with the rate of flow or more properly the rate of shear. The log h versus t plot gives a curve with m varying from point to point. This variation can be utilized to relate the wall shear rate γ_w to the wall shear stress τ_w from which a flow curve τ_w versus γ_w can be constructed. An approach similar to that developed by Krieger and Maron [3] is employed.

The experiment described in this report provides for student exposure to non-Newtonian flow as well as computer aided data analysis. Several types of fluids can be employed to illustrate types of flow behavior.

First, an effective fluidity is defined, with reference to equation (2) as

$$\phi_e = \frac{1}{\eta_e} = \frac{8LQ}{\pi R^4 \Delta P} \tag{6}$$

where η_e is the effective viscosity. From the expressions in equation (5) it can be seen that ϕ_e is given by

$$\phi_e = - \frac{m}{B\rho} \tag{7}$$

Under conditions of steady, laminar flow of a time-independent fluid through a cylindrical tube, it can be readily shown [4, 5] that

$$\frac{Q}{\pi R^3} = \frac{1}{\tau_w^3} \int_0^{\tau_w} \tau^2 f(\tau)\, d\tau \tag{8}$$

where

$$\tau_w = \frac{R\Delta P}{2L} \quad ; \quad f(\tau) = \dot{\gamma} \tag{9, 10}$$

Combination of equations (6), (8), and (9) gives

$$\phi_e = \frac{4Q}{\pi R^3 \tau_w} = \frac{4}{\tau_w^4} \int_0^{\tau_w} \tau^2 f(\tau)\, d\tau \tag{11}$$

Differentiation of equation (11) with respect to τ_w using Leibnitz's rule and rearrangement of the result gives

$$\frac{\dot{\gamma}_w}{\tau_w} = \phi_e \left(1 + \frac{1}{4} \frac{d \ln \phi_e}{d \ln \tau_w}\right) \tag{12}$$

The terms in ϕ_e and τ_w in equation (12) are replaced by equations (7) and (9) so that after some algebais manipulation equation (12) becomes

$$\frac{\dot{\gamma}_w}{\tau_w} = - \frac{m}{B\rho} \left(1 + \frac{1}{4m^2} \frac{dm}{dt}\right) \tag{13}$$

Equation (13), coupled with equation (9), is used to determine the flow curve of a non-Newtonian fluid.

DATA ANALYSIS

THE AVERAGE OF the x versus time data is first converted into h versus t with the aid of equation (1). Equations (3) and (9) give the wall shear stress

$$\tau_w = \frac{R \rho g h}{2L} \tag{14}$$

which can be readily evaluated. To evaluate the wall shear rate from equation (13) values for m and dm/dt are required. This information can be obtained from the h versus t data with the aid of a non-linear parameter estimation technique (Bard's method [6]). Bard's method is in the form of a computer program provided by IBM. The user must supply the mathematical model, initial guesses and the bounds on the parameters, and the experimental data. The outputs include the estimated parameter values and the deviation of computed values from observed data values. From the deviation one can judge how well the proposed model fits the data points.

From the data examined, it appears that the h versus t data can be described by a function of the form

$$h = h_o \exp \{-kt + (a + b\, t)^c\} \tag{15}$$

where

h_o = h value when t equals to zero (measured)

k, a, b, c = parameters to be estimated

The parameters a, b and c in equation (15) result from the non-linearity of a ln h versus plot. For the initial guesses of the parameters, k can be taken as the negative value of the slope of a line fitting the first few points of the ln h versus t plot. An initial guess for the parameter c is taken as 2. The parameters a and b can then be estimated as the intercept and the slope of the least-square-fit line of a $\sqrt{\delta}$ versus t plot, respectively, with δ defined by*

$$\delta = \ln h - \ln h_o + kt \tag{16}$$

Only a rough estimation for these parameters is sufficient and this can be easily done on a programmable desk calculator, or available computer program such as the IBM scientific subroutines package.

Both upper and lower bounds must be supplied in the input. The determination of these bounds is somewhat arbitrary. The bounds as suggested from this study are the following,

1) k: initial guess x (1.00 ± 0.30) (17a)

2) a: $0 < |a| < 0.1$ (17b)

3) b: $0 < b < 0.01$ (17c)

4) c: $1 < c < 5$ (17d)

where the upper bounds of |a| and b are arbitrarily chosen as one order of magnitude greater than the values ordinarily encountered.

The parameters estimated by the computer program can be used to analytically evaluate m and dm/dt. From equation (15),

$$m = \frac{d \ln h}{dt} = -k + cb(a + bt)^{c-1} \tag{18}$$

From equation (18), dm/dt results,

$$\frac{dm}{dt} = c(c-1)\,b^2\,(a + bt)^{c-2} \tag{19}$$

For the special case of slight curvature of the ln h versus t data one can generally obtain a satisfactory description of the data by setting c = 2. This reduces the computer time required and eliminates one parameter from the parameter estimation. Substitution of equations (18) and (19) into equation (13) gives an expression for γ_w/τ_w in terms of the parameters. The evaluation of m, dm/dt, τ_w, and γ_w/τ_w can be done on the computer with a slight addition to the original Bard's program. In this way, the flow curve information, τ and γ, is obtained directly as computer output. A print-out of the program can be obtained by writing the authors.

*It is apparent that δ represents the deviation of a ln h versus t plot from linearity. This deviation usually is a quadratic function of t. Accordingly, equation (15) was formulated.

Table 1. Results for the test fluid

Time, t (sec)	$h_{exp'l}$ (cm)	ln $h_{exp'l}$	δ	$\delta^{1/2}$	$h_{cal'd}$ (cm)	τ (dyne/cm^2)	$\dot{\gamma}$ (sec^{-1})
0	56.50	4.0342	0	0	56.54	74.8	1303
7.7	55.44	4.0153			55.45	73.4	1276
23.4	53.31	3.9762			53.31	70.5	1223
39.8	51.19	3.9355			51.18	67.7	1169
56.8	49.07	3.8932	0	0	49.06	64.9	1116
74.8	46.94				46.93	62.1	1063
93.6	44.82				44.80	59.3	1011
113.2	42.69				42.70	56.5	959
134.4	40.57				40.55	53.6	906
156.6	38.45	3.6492	.002	.04	38.42	50.8	854
205.1	34.20				34.19	45.2	751
231.9	32.07				32.08	42.4	700
246.2	31.03				31.01	41.0	675
251.0	29.95	3.3995	.007	.08	29.95	39.6	649
276.5	28.89				28.87	38.2	624
292.4	27.83				27.82	36.8	599
309.2	26.76				26.75	35.4	573
326.3	25.70				25.68	34.0	548
345.1	24.64	3.2044	.017	.13	24.62	32.5	523
364.1	23.58				23.56	31.2	498
384.2	22.52				22.51	29.8	473
427.3	20.39				20.41	27.0	425
450.9	19.33	2.9616	.032	.18	19.35	25.6	400
475.9	18.27				18.30	24.2	376
502.5	17.21				17.25	22.8	352
531.2	16.14				16.20	21.4	328
564.3	15.08				15.07	19.9	303
596.7	14.02	2.6405	.064	.25	14.05	18.6	280
633.9	12.96				12.97	17.2	256
674.5	11.90				11.90	15.8	232
719.2	10.83				10.84	14.3	209
769.9	9.77				9.76	12.9	186
828.4	8.71	2.1645	.143	.38	8.67	11.5	162
896.0	7.65				7.58	10.0	139

AN EXAMPLE OF THE METHOD

PRESSURE FLOW DATA (in the form of h versus t) for a non-Newtonian fluid are used to illustrate the procedure. The fitted h versus t curve is then compared with experimental values. The best fit parameters are then employed for the determination of the flow curve for the fluid. For this example, it was assumed that c = 2.

Reference is made to Table 1. Column 2 gives the h values converted from raw data of x versus t by equation (1). Column 3 presents ln h values which are used for the initial guess of k. A least square fit of these data in the form of ln h_{expl} versus t is made with a programmable Wang calculator. The result for this case gives a slope of —0.0024819. Hence the initial guess of k is taken as 0.0024819. Values of δ are then calculated as

Table 2. Values for various parameters

	k	a	b
initial guess	0.0024819	-0.031137	0.00049889
lower bound	0.0017373	-0.1	0.
upper bound	0.0032265	0	0.01
estimated parameter	0.0024855	-0.025336	0.00054924

indicated by equation (16). The values of δ and $\sqrt{\delta}$ are tabulated in columns 4 and 5. The $\sqrt{\delta}$ data are used for the initial guesses of parameters a and b. The ($\sqrt{\delta}$ versus t) data are fitted by least squares with the aid of a programmable calculator. The resulting intercept and slope give the initial guesses of a and b, respectively. These values are presented in Table 2. Bounds for parameters calculated by the program are also shown in Table 2. These parameter values are used in the program to calculate h values by equation (15). The resulting h values are presented in column 6 of Table 1. A comparison between the best fit curve and the experimental data is given in Fig. 2. As can be seen from the figure the fitted

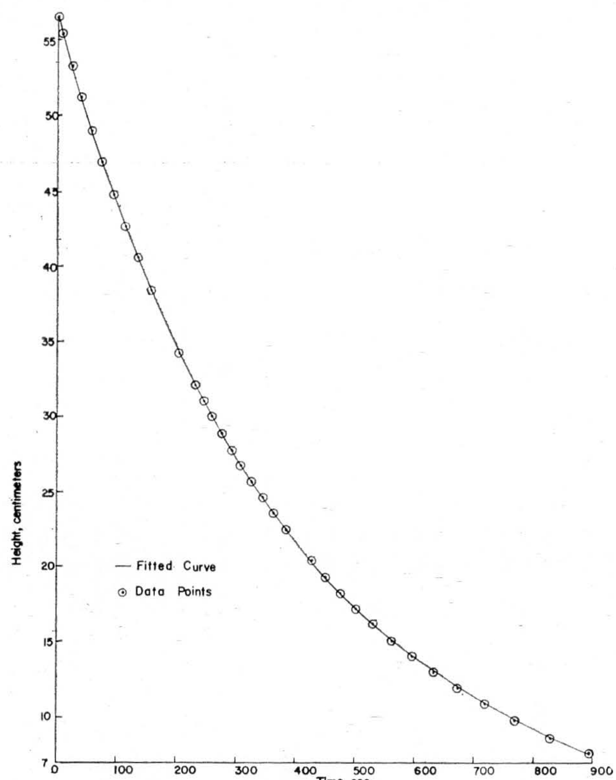

Fig.2. A typical fitted curve for h vs. t data.

curve describes the experimental points very well. The error in h_{cald}, as can be seen in Table 1, never exceeds 1%.

Next τ_w and γ_w, as given by,

$$\tau_w = \frac{R\rho g h}{2L} \quad ; \quad \text{and} \quad \dot{\gamma}_w = \tau_w \cdot \frac{-m}{B\rho}\left\{1 + \frac{1}{4m^2}\frac{dm}{dt}\right\} \qquad (15, 13)$$

are evaluated, using the estimated parameters. Here h, m and dm/dt are given in terms of the parameters by equations (15), (18) and (19).

The results are shown in column 7 and 8 of Table 1 as well as in figure 3. As shown in Fig. 3. the shear rate range from a single determination covers about one cycle. The flow curve of non-unit slope indicates the non-Newtonian behavior of the test-fluid.

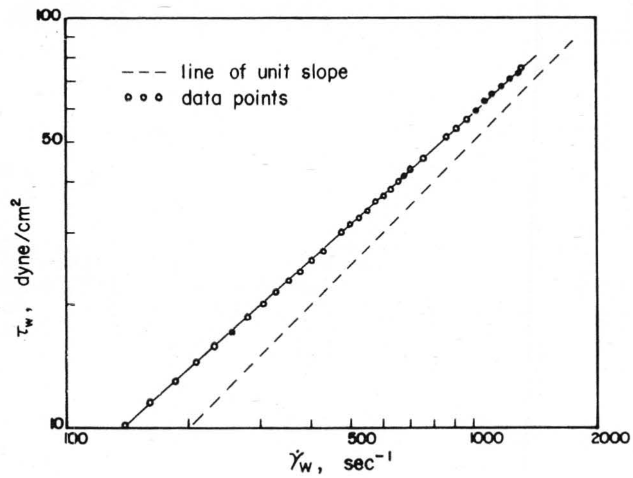

Fig.3. The flow curve.

STUDENT RESULTS

SEVERAL STUDENTS conducted the experiment with a 0.05% (wt) solution of CMC in water. The capillary employed was 19.88 cm long and had an inside diameter of 0.1020 cm. Reproducibility of the raw data (x vs t) was quite good with agreement within ½% on the total flow time of approximately 750 seconds. For this fluid, the parameter c could not be taken as 2 and was estimated along with the other parameters. A typical h versus t curve is shown in Fig. 4. As can be seen the agreement is quite good. A typical flow curve is shown in Fig. 5. For the CMC sample employed, one can observe the trend towards the "zero shear" limiting viscosity by replotting the data in the form of η versus γ ($\eta = \tau/\gamma$).

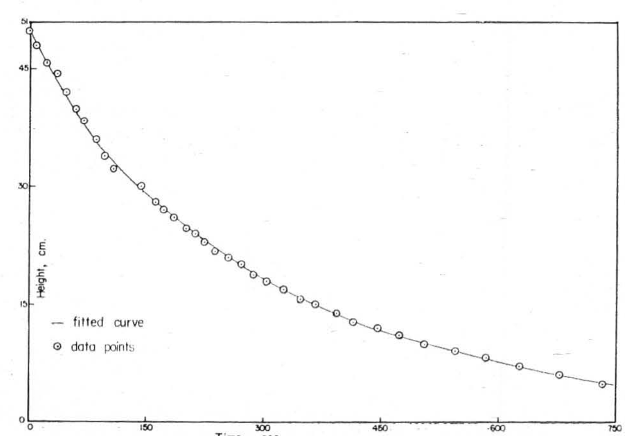

Fig 4. H. vs. t curve

SUMMARY

IN SUMMARY THE experiment described in this report provides for student exposure to non-Newtonian flow as well as computer aided data analysis. Several types of fluids can be employed to illustrate the various types of flow behavior. In utilizing this experiment it is suggested that several diameters of capillary be available in order to ensure reasonable experiment length (total flow time) as well as to provide for greater variation in shear rate. □

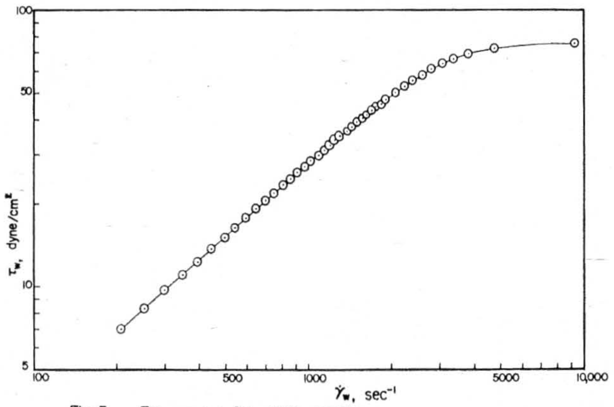

Fig. 5. Flow curve for CMC solution.

ACKNOWLEDGMENT

This work was supported in part by a grant from Kansas Heart Association #KR-72-10. This support is gratefully acknowledged. The efforts of the junior Chemical Engineering students (1973-74) in testing the experiment are greatly appreciated.

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APPENDIX

A printout of the computer program is available. It consists of seven decks; a main program and six subroutines. Definitions of the variables added are given in the comment statements. Names of the other subroutines are given to show the entire structure of the program. For details of the entire technique, reference can be made to Bard's original manual [6].