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Effect of Corn Stover Concentration on Rheological Characteristics

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Abstract

Corn stover, a well-known example of lignocellulosic biomass, is a potential renewable feed for bioethanol production. Dilute sulfuric acid pretreatment removes hemicellulose and makes the cellulose more susceptible to bacterial digestion. The rheologic properties of corn stover pretreated in such a manner were studied. The Power Law parameters were sensitive to corn stover suspension concentration becoming more non-Newtonian with slope n, ranging from 0.92 to 0.05 between 5 and 30% solids. The Casson and the Power Law models described the experimental data with correlation coefficients ranging from 0.90 to 0.99 and 0.85 to 0.99, respectively. The yield stress predicted by direct data extrapolation and by the Herschel-Bulkley model was similar for each concentration of corn stover tested.

Index Entries: Corn stover; rheological measurement; shear stress; shear rate; non-Newtonian fluids; Power Law parameters.

Introduction

The production of fuel ethanol from renewable lignocellulosic material ("bioethanol") has the potential to reduce world dependence on petroleum and to decrease net emissions of carbon dioxide. The lignin-hemicellulose network of biomass retards cellulose biodegradation by cellulolytic enzymes. To remove the protecting shield of lignin-hemicellulose and make the cellulose more readily available for enzymatic hydrolysis, biomass must be pretreated *(1)*.

Thermochemical treatment, such as with steam and dilute sulfuric acid, is a popular pretreatment process. This treatment opens the lignocellulosic pore structure and increases the susceptibility of biomass to enzymatic attack *(2)*. This pretreatment step effectively hydrolyzes the biomass,

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yielding liquor typically rich in pentose sugars and generating a cellulose-rich solid with greater porosity and improved enzymatic digestibility *(2)*.

Stirred tanks are typically used for the thermochemical pretreatment. To simulate flow of corn stover slurries in stirred tanks, the rheologic properties of these suspensions must be known. The corn stover slurries in stirred tank reactors typically range from 10 to 40% solids *(3)*.

In systems with suspended solids, rheologic measurements are difficult to perform owing to settling in the measurement devices. Conventional methods for measuring rheologic properties (cone-and-plate, concentric cylinder, and rotating-bob viscometers) do not produce accurate and reliable data for some solid suspensions.

To avoid the apparent complications with absolute rheologic measurement techniques, a number of investigators *(4,5)*. have used relative measurement systems to make rheologic measurements. The major difference between the relative and absolute measurement techniques is that the fluid mechanics in the relative systems are complex. The constitutive equations needed to find the fundamental rheologic variables cannot be readily solved. Relative measurement systems require the use of Newtonian and non-Newtonian calibrations fluids with known properties to relate torque and rotational speed to the shear rate and shear stress *(6)*.

Research on the impeller method using the helical ribbon impeller is well documented *(7,8)*. The impeller method is often employed to measure the rheology of suspensions. Previous researchers assumed that the effective shear rate of such a device is related to the impeller speed by a fluid-independent constant, but this assumption may not be accurate for all impellers *(8,9)*. It has been suggested that a properly designed helical ribbon impeller might be more appropriate for this technique.

Yield stress can be determined by indirect and direct methods. The indirect method consists of curve fitting the experimental shear stress–shear rate data to rheologic models with a yield stress term. Accurate data are essential at lower shear rates to obtain reliable results. A direct method, such as the stress growth method, relates the yield stress to the maximum torque registered in a shear stress–time response. The goal of the present investigation was to determine the rheologic properties of dilute-acid-pretreated corn stover suspensions using the impeller method and to determine the yield stress of these suspensions using the indirect and direct methods.

Data Analysis for Impeller Viscometer Technique

The complex flow field created by the impeller does not allow the direct calculation of shear rate *(6,8)*. It is assumed that the dimensionless power number (p_{No}) is inversely proportional to the impeller Reynolds number (Re_i) for Newtonian fluids in a laminar flow regime in which the RE_i is <10:

$$p_{No} = c/Re_i = \frac{2\pi M}{\rho N^2 D_i^5} \text{ for } Re < 10 \quad (1)$$

$$Re_i = \frac{\rho N D_i^2}{\mu} \tag{2}$$

in which c is an empirically determined constant, M is the torque, D_i is the diameter of the helical impeller, and ρ is the density of the fluid.

For a given impeller, the torque is directly proportional to the impeller speed and the apparent viscosity:

$$M = \frac{cD_i^3}{2\pi}\mu N \tag{3}$$

If the torque is measured as a function of the impeller speed for a known-viscosity Newtonian fluid, the constant, c, can be determined. The apparent viscosity for a non-Newtonian fluid can then be determined from measurements of the impeller torque as a function of impeller speed from Eq. 3 *(7)*.

Replacing the viscosity, μ, in the Re_i with the apparent viscosity of the non-Newtonian fluid, η_a, at the average shear rate, and solving Eq. 2 for the apparent viscosity produces

$$\eta_a = \frac{2\pi M}{cND_i^3} \tag{4}$$

The "average" shear rate in the measuring vessel, γ_{avg}, is assumed to be proportional to the impeller speed, N, and independent of the rheology of the fluid in the vessel. The shear rate constant, k, is used as a fluid-independent constant:

$$\gamma_{avg} = kN \tag{5}$$

If this approach is valid, the shear rate constant can be determined from experimental measurements of torque vs impeller speed for non-Newtonian fluids of known properties *(10)*.

The apparent viscosity is determined from Eq. 4. The value of shear rate that corresponds to this viscosity is obtained from the known viscosity vs shear rate rheogram for the non-Newtonian fluids generated using the cone-and-plate method. The value of k is determined from Eq. 5.

Yield Stress

Yield stress is defined as the shear stress that has to be applied before the material starts to flow. Nguen and Boger *(11)*. indicated that the yield stress can be measured by either indirect or direct methods. Indirect methods consist of either using rheologic models to fit the shear stress–shear rate experimental data or extrapolating the shear stress–shear rate data to zero shear rate. Direct methods involve shearing a fluid in a rotational viscometer at a low and constant shear rate and measuring the shear stress as a function of time. The stress-vs-time (or shear strain) response typically consists of an initially linear portion indicating elastic solid behavior, followed by a nonlinear region, a stress overshoot, and a stress decay region *(11)*.

Indirect determination of the yield stress simply involves extrapolation of the experimental shear stress–shear rate data to obtain the yield value as the shear stress limit at zero rate of shear. The extrapolation is performed numerically on the available data, or the latter can be fitted to a suitable rheologic model representing the fluid, and the yield stress parameter in the model is determined.

A more convenient extrapolation technique is to approximate the experimental data with a viscosity model. The Power Law, shown in Eq. 6, is the most commonly used two-parameter model. The Bingham model, shown in Eq. 7, postulates a linear relationship between τ and γ but can lead to overprediction of the yield stress. Extrapolation of the nonlinear Casson model (1954), shown in Eq. 8, is straightforward from a linear plot of $\tau^{0.5}$ vs $\gamma^{0.5}$. Application of the Herschel-Bulkley model (1926), shown in Eq. 9, is more tedious and less certain although systematic procedures for determining the yield value and the other model parameters are available *(11)*:

$$\tau = K_{pl}(\gamma)^{n} \tag{6}$$

$$\tau - \tau_y^B = \eta_p \gamma \tag{7}$$

$$\tau^{0.5} = \left(\tau_y^c\right)^{0.5} + \eta^c (\gamma)^{0.5} \tag{8}$$

$$\tau = \tau_y^{HB} + K^{HB}\gamma^{n_{HB}} \tag{9}$$

Materials and Methods

Equipment

Two Brookfield rheometers with full-scale spring torques of 7178 and 57,496 dyne-cm were used: a digital RV-DV III cone-and-plate instrument and a digital HB-DV III, respectively. The uncertainty specified by the manufacturer for these devices is 1% of the full-scale range. Therefore, no data were taken unless the torque displayed was >5% of the maximum value for a given instrument. A cone/plate attachment (RV-DV III viscometer) was used to characterize the rheology of the Newtonian and non-Newtonian calibration fluids used (Brookfield spindle cp-42). The temperature was maintained at 25.0 ± 0.1°C for all tests using a circulating water bath.

The helical impeller was fashioned from nylon using selective laser sintering technology and is shown in Fig. 1. It had a diameter of 0.04 m and a pitch of 0.02 m. The impeller featured two helices, an ascending outer flight and a descending inner flight. The length of the impeller was 0.055 m, and it was located at an off-bottom clearance of 0.025 m.

The use of Newtonian and non-Newtonian calibration fluids allows the determination of constants relating the measured torque and speed to viscosity and shear rate. Silicone oil and glycerin (Newtonian) with viscosities of 1.024 and 0.912 Pa·s, respectively, were used to determine the impeller constant, *c*, while xanthan and guar gum solutions (non-Newtonian) were used to determine the shear rate constant, *k*.

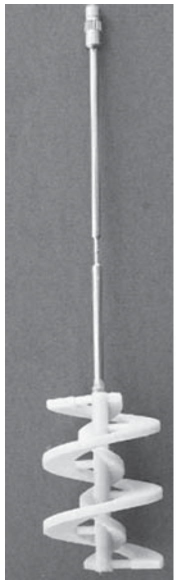

Fig. 1. Helical impeller.

Corn Stover Suspensions

The corn stover suspensions used were composed of various concentrations of corn stover particles (average fiber length = 120 μm) suspended in water. The National Renewable Energy Laboratory (NREL) provided the pretreated corn stover used to prepare the corn stover suspensions. This corn stover was pretreated in a 1.4% sulfuric acid solution for 3–12 min and then dewatered. It contained byproducts of the pretreatment process including lignocellulosic sugars, sulfuric acid, and acetic acid. To prepare samples for viscosity testing, the pretreated corn stover was dried and then reconstituted to the desired concentration by adding deionized water.

Rheologic Measurements

Rheologic measurements were performed at 25oC with the cone-and-plate and helical impeller viscometers. Impeller viscometer measurements were performed in a 1000-mL beaker with a diameter of 0.115 m. A liquid height of 0.115 m was used for all tests.

For the impeller ribbon viscometer technique, the power number of an impeller is inversely proportional to the impeller Reynolds number (Eq. 1). As the impeller rotational speed increases, the flow will gradually change from laminar to turbulent, passing through a transition region. Parameter c can be obtained from the calibration fluids. If the same value for c is assumed to apply to a non-Newtonian fluid, then Eq. 4 can be used to calculate the apparent viscosity of that fluid. The range of the impeller method is determined by the minimum and maximum torques that can be measured *(5)*.

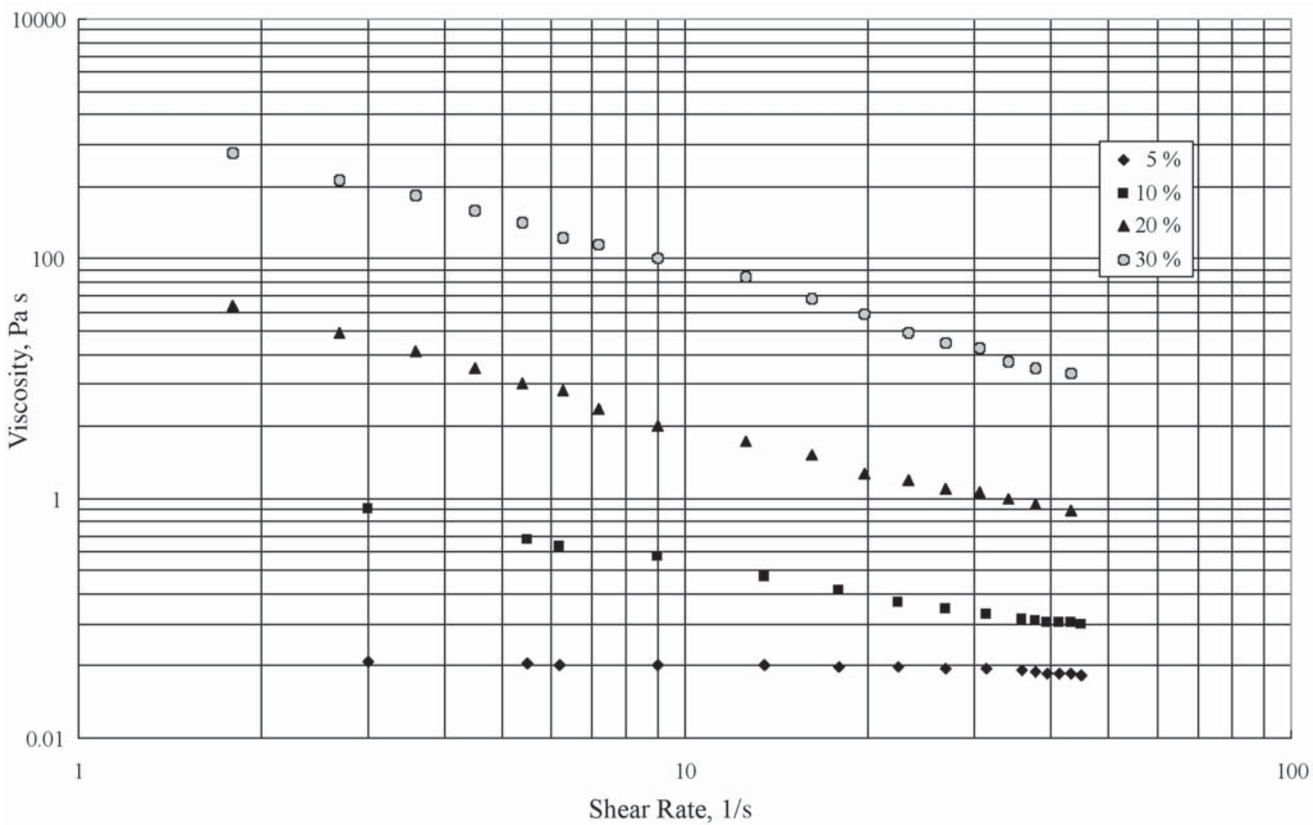

Fig. 2. Viscosity vs shear rate for corn stover suspensions between 5 and 30 wt%.

Table 1
Power Law Parameters for Corn Stover Suspensions

Corn stover concentration (%)	K_{pl} (Pa·s)	n	R^2
5%	0.05	0.91	0.90
10%	1.87	0.08	0.99
20%	71.82	0.06	0.99
30%	1684.5	0.05	0.99

Yield Stress

The indirect method can be employed by extrapolating the rheologic models or the shear stress–shear rate data to zero shear rate. The computer software Table Curve 1.12 was used to fit the shear stress–shear rate data to the different rheologic models. This software uses the Simplex method for a nonlinear regression curve fit.

Results

Determination of Viscosity

Using Newtonian calibration fluids the value for the constant, c, was determined to be 135 *(12)*. The deviation in the value of c between Reynolds numbers from 1 to 10 was <5%.

The value of the shear rate constant, k, was determined for solutions of xanthan gum and guar gum with concentrations of 0.5, 1.0, and 1.5%. The shear rate constant k obtained from the cone-and-plate and helical impeller was 10.9. A similar value of k was obtained for 1.0 and 1.5% of xanthan and guar gum solutions. The same value of k was reported for this type of impeller in earlier investigations *(7,9)*.

The results of the rheologic measurements for the corn stover suspensions of 5, 10, 20, and 30% are presented in Fig. 2. The viscosity of the suspension increased as the fiber loading increased.

Power Law Parameters

The consistency index constant, K_{pl}, and the consistency index number, n, were calculated for all corn stover suspensions, using linear regression. The results are presented in Table 1. All of the regression coefficients are above 0.99. The parameters are independent of the method of measuring rheologic data and dependent on the fluid.

Yield Stress

Indirect Methods

Four models (Power Law, Herschel-Bulkley, Casson, and Bingham) were used to fit the experimental data and to determine the yield stress of

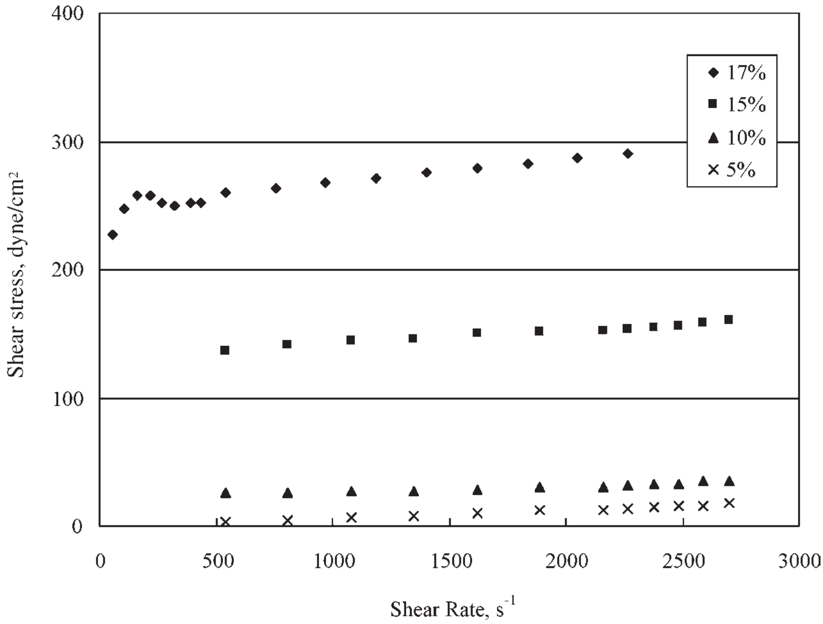

Fig. 3. Shear stress vs shear rate for 5, 10, 15 and 17% corn stover suspensions.

the solution. Figure 3 illustrates shear stress vs shear rate data for 5, 10, 15, and 17% corn stover suspensions; Table 2 lists the yield stress values determined by extrapolation of the shear stress vs shear rate data. Figure 4 shows the experimental data and the four rheologic models used to fit the data; Table 3 lists the fitted parameters for the corn stover suspensions at the various concentrations.

Direct Methods

Yield stress measurements were performed with corn stover suspensions in mass concentrations ranging from 5 to 17 wt%. Less concentrated suspensions did not draw sufficient torque to permit reliable yield stress measurements. To demonstrate the difficulty of obtaining meaningful rheologic data using conventional rotational viscometers, the stress growth method was applied to directly measure the yield stress of 5% corn stover suspension. The stress growth method is not suited for measuring yield stress for filamentous suspensions because of particle settlement. Conventional viscometers are not able to cope with the filamentous nature of the suspensions. The long filaments tend to block the gap between the cone and the plate. Furthermore, using the cone- and-plate viscometer in the stress growth method requires 1- or 2-mL fluid samples depending on the spindle used. Because of the filamentous nature of the solution, it is difficult to be sure that the sample placed in the cup contains the correct concentration of fibers. Solid particles would tend to separate out of the suspension, causing a lower concentration of the solid in the test fluid.

Table 2
Yield Stress Values for Corn Stover Suspensions
Determined with Shear Stress vs Shear Rate Data Extrapolation

	wt%			
	5	10	15	17
Yield stress (Pa)	0.26	2.57	12.7	22.9

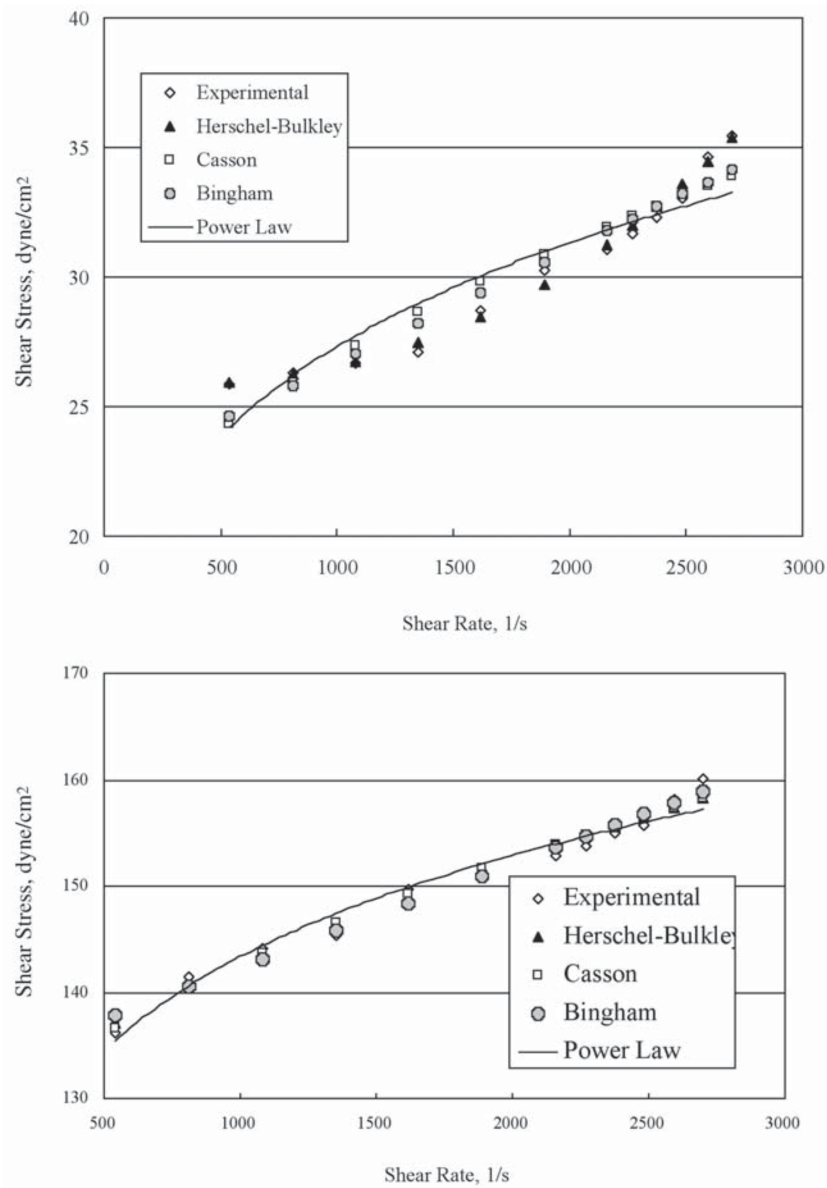

Fig. 4. Rheologic models used to fit shear stress vs shear rate data calculated from impeller method for 10 and 15% corn stover suspensions.

Table 3
Results for Indirect Yield Stress Determination for Corn Stover Suspensions in 1.0-L Beaker (Helical Impeller Method)

wt%	Model fitted	τ (Pa)	K (Pa·s^n)	n	R^2
5	Herschel-Bulkley	τ_y^{HB}: 0.152	K^{HB}: 0.001	n_{HB}: 1.13	0.985
	Casson	τ_y^c: 0	η_c: 0.081	0.50	0.993
	Bingham	τ_y^B: 0.089	η_P: 0.006	—	0.992
10	Herschel-Bulkley	τ_y^{HB}: 2.42	K^{HB}: 2.5×10^{-8}	n_{HB}: 0.87	0.991
	Casson	τ_y^c: 2.08	η_c: 0.031	0.50	0.900
	Bingham	τ_y^B: 2.23	η_P: 0.004	—	0.938
15	Herschel-Bulkley	τ_y^{HB}: 12.77	K^{HB}: 0.0912	n_{HB}: 0.736	0.982
	Casson	τ_y^c: 12.03	η_c: 0.031	0.50	0.981
	Bingham	τ_y^B: 13.26	η_P: 0.0097	—	0.979
17	Herschel-Bulkley	τ_y^{HB}: 22.9	K^{HB}: 1.573	n_{HB}: 0.722	0.917
	Casson	τ_y^c: 23.196	η_c: 0.037	0.50	0.917
	Bingham	τ_y^B: 24.553	η_P: 0.02045	—	0.891

Finally, the distribution of solid particles across the gap may not be uniform if the fibers separated out of the suspension. Therefore, based on the previous reasoning, it is concluded that the stress method does not offer a reliable and accurate way to measure yield stress in filamentous suspensions. Figure 5 shows the typical torque-time relationship obtained with the helical impeller method for corn stover suspensions.

Discussion

Calibration Procedure

The basic assumption of the impeller viscometer approach is that the shear rate constant is independent of the rheologic properties of the fluid. This assumption allows the helical impeller viscometer to be calibrated using Newtonian and non-Newtonian fluids. The calibration results for guar and xanthan gum solutions ranging in concentration from 0.5 to 1.5% produced a single value of $k = 10.8$, which is sufficient to represent all the data.

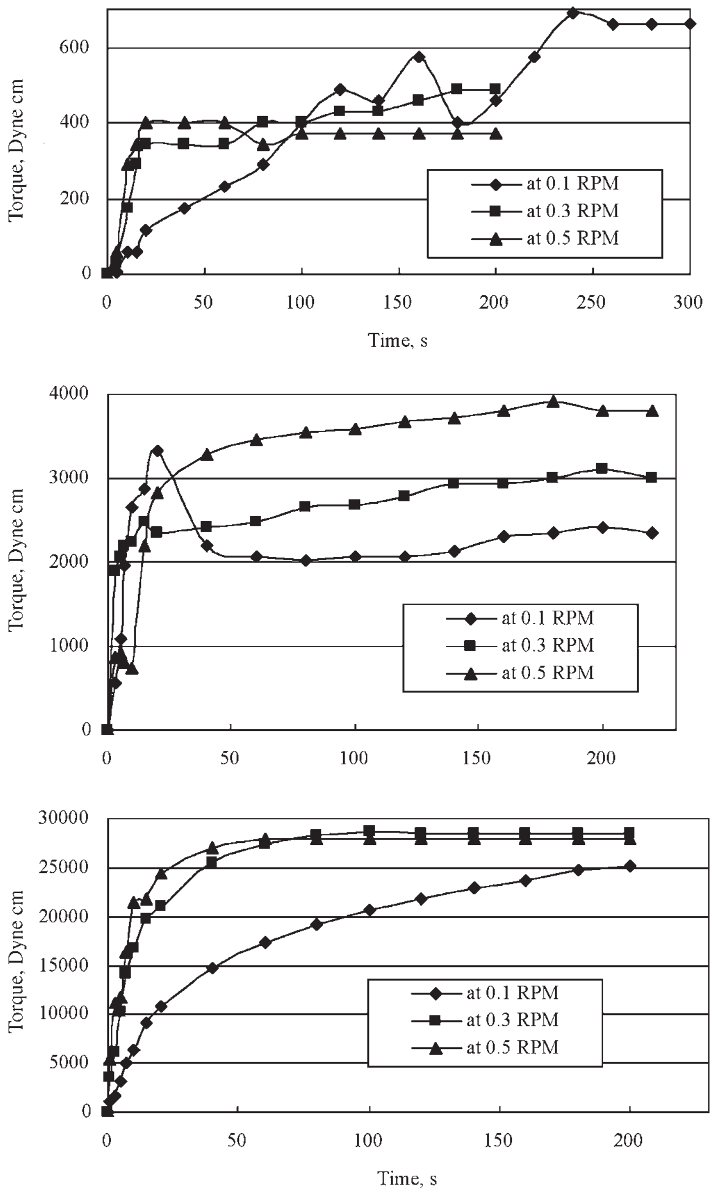

Fig. 5. Torque vs time for 5, 10, and 15% corn stover suspensions.

Corn Stover Suspensions

The viscosity of the corn stover suspensions was determined for concentrations up to 30%. The helical impeller method was ineffective above corn stover concentrations of 32%.

The Power Law parameters for the corn stover suspensions could not be located in previous studies. Dronawat *(13)*. studied a similar system using filamentous particles (Solka-Floc with a fiber length 215 µm in a 0.5% xanthan gum water solution). Comparison of the Power Law parameters indicates that the suspensions studied here were less viscous and less shear thinning than the suspensions Dronawat studied. The difference can be attributed to the fact that the present study used water rather than a 0.5% of xanthan gum solution. In both studies the increase in the consistency index as the Power Law index increased was moderate.

Shear Stress vs Shear Rate

The relationship between shear stress and shear rate is also an indication of the degree of Newtonian behavior that a fluid exhibits. The linearity of the relationship is a direct indication of Newtonian behavior. The 5% corn stover suspension exhibited Newtonian behavior; the remaining corn stover suspensions exhibited non-Newtonian behavior. At the other concentrations (>5%), the degree of linearity decreased with increasing mass concentration. Figure 4 illustrates the non-Newtonian characteristics of the remaining corn stover suspensions.

Yield Stress

Various techniques have been devised for measuring the yield stress directly and independently of the basic shear stress–shear rate data. Although the general principle of the yield stress as the stress limit between flow and nonflow conditions is often used, the specific criterion employed for defining the yield stress seems to vary among these techniques. Furthermore, each technique appears to have its own limitations and sensitivity so that no single one can be considered versatile or accurate enough to cover the whole range of yield stress and fluid characteristics.

Cone- and-plate stress growth experiments are sensitive to torque deflections in the measuring spring. This effect was more pronounced at higher guar gum concentrations owing to the high viscosity of the solutions. The stress growth method can be ineffective in measuring yield stress for filamentous suspensions, such as corn stover suspensions. The solid particles can block the gap between the cone and plate, hampering any reliable rheologic measurement. Nguen *(11)* wrote that determination of yield stress from the stress growth method is doubtful since lower and upper yield stress values may be obtained. As reported by Joch *(14)*, the values determined herein correspond to the upper, or overshoot, yield stress. The lower yield stress is reported to be the point where the fluid changes from elastic to plastic behavior; the upper yield stress is where the fluid changes from plastic to viscous behavior. When the structure of the fluid has been broken, the fluid has made the transition from plastic to viscous behavior.

The helical impeller technique is better suited to measure yield stress in a greater variety of fluids, including filamentous suspensions. The helical impeller technique is also less sensitive to initial undesired torque deflections in the measuring spring. The undesired initial torque, introduced at the moment the helical impeller is submerged into the liquid, can easily be minimized by slowly and gently rotating the vessel in the proper direction to compensate for the initial torque. This procedure worked best in moderate to very viscous solutions, since rotation of the vessel for more dilute solutions did not exert enough drag on the helical impeller.

Comparison of the curves in Fig. 5 gives a clear indication of the difficulty involved in working with corn stover suspensions. At some concentrations and rotational rates, the curves show a well-defined maximum followed by a region where torque became independent of time. At other concentrations and rotational rates, the curves show a well-defined global maximum followed by various local maxims. These local peaks can be a consequence of particle settling during the experiment. The experiments using the helical impeller method were 400 s in duration to allow sufficient time for a change in the extent of dispersion of the solids throughout the vessel.

The yield stress values given in Table 3 demonstrate that the yield stresses determined with the Herschel-Bulkley model were lower than the yield stresses determined with all the other methods at equal concentrations. The yield stress predicted by direct data extrapolation and by the Herschel-Bulkley model was similar for each concentration of corn stover.

Conclusions

The parameter c was found to be a linear function of Reynolds number with regression coefficients between 0.98 and 1.00. The shear rate constant, k, was within 10% of the values found by Donnelly *(15)* and Rieth *(16)* for a double-helical ribbon impeller. Furthermore, the Power Law could be used to describe corn stover suspension viscosity with correlation coefficients above 0.99 for all four concentrations tested. Finally, the yield stress predicted by direct data extrapolation and by the Herschel-Bulkley model was similar for each concentration of corn stover.

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