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Measurement of Rheological Properties of Corn Stover Suspensions

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Abstract

Corn stover is currently being evaluated as a feedstock for ethanol production. The corn stover suspensions fed to reactors typically range between 10 and 40% solids. To simulate and design bioreactors for processing highly loaded corn stover suspensions, the rheologic properties of the suspension must be measured. In systems with suspended solids, rheologic measurements are difficult to perform owing to settling in the measurement devices. In this study, viscosities of corn stover suspensions were measured using a helical ribbon impeller viscometer. A calibration procedure is required for the impeller method in order to obtain the shear rate constant, *k*, which is dependent on the geometry of the measurement system. The corn stover suspensions are described using a power law flow model.

Index Entries: Corn stover; rheological properties; helical impeller; cone-and-plate impeller; power law parameters.

Introduction

Production of fuel ethanol from renewable lignocellulosic material (bioethanol) has the potential to reduce world dependence on petroleum while decreasing net emissions of CO_2, the principal greenhouse gas. Lignocellulosic biomass includes hardwoods, herbaceous crops, agricultural residues (i.e., corn stover), and wastepaper and other fractions of municipal solid waste. These materials are primarily cellulose, hemicellulose, and lignin *(1–3)*.

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 *(4)*.

Thermochemical treatment (e.g., with steam and dilute H_2SO_4) is a popular pretreatment process. This treatment opens the lignocellulose pore

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structure and increases the susceptibility of biomass to enzymatic attack *(1)*. This pretreatment step effectively hydrolyzes liquor typically rich in pentose sugars and produces a cellulose-rich solid with greater porosity and improved enzymatic digestibility *(1)*.

Stirred tanks are usually 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 *(5)*.

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. Common problems encountered with conventional instruments include phase separation near the vicinity of the bob, particle settling, destruction of particles in the vicinity of the rotating device, and blockage of narrow gaps by large particles *(6,7)*.

To avoid the apparent complications with absolute rheologic measurement techniques, a number of investigators *(8,9)* 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 calibration fluids with known properties to relate torque and rotational speed to the shear rate and shear stress *(10)*.

Research on the impeller method using the helical ribbon impeller is well documented *(6,7)*. 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 there is evidence that this is not true for all impellers *(7,11)*. It has been suggested that a properly designed helical ribbon impeller might be more appropriate for this technique.

The principal goal of the present investigation was to study the rheology of corn stover slurries. The objectives were to determine the effectiveness of the impeller method in measuring the rheologic properties of corn stover slurries, to determine the power law parameters of suspensions with different concentrations of corn stover fiber using the impeller method, and to compare the power law parameters of the corn stover slurries with those of filamentous suspensions reported in the literature.

Data Analysis for Impeller Viscometer Technique

The complex flow field created by the impeller does not allow direct calculation of the shear rate *(7,10)*. 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:

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

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

in which k and c are empirically determined constants, M is the torque, D_i is the diameter of the helical impeller, and ρ is the density of the using 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 *(6)*.

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 *(12)*.

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.

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 instru-

Fig. 1. Helical impeller.

ment 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 using a circulating water bath for all tests.

The helical impeller used was fashioned from nylon using selective laser sintering technology (*see* Fig. 1). The impeller had a diameter of 0.04 m and a pitch of 0.02 m and 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 determination of constants relating the measured torque and speed to viscosity and shear rate. Silicone oil and glycerol (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*.

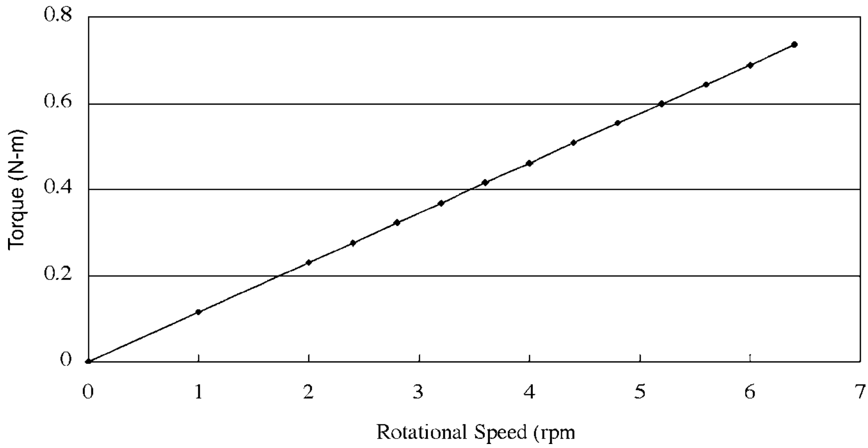

Fig. 2. Torque-speed relationship for Newtonian silicone oil.

Corn Stover Suspensions

The corn stover suspensions used were composed of various concentration of corn stover particles (average fiber length = 120 μm) suspended in water. Corn stover liquor was used to prepare corn stover suspensions. Cooking corn stover in a 1.4% H_2SO_4 solution and then dewatering the resultant slurry produced corn stover liquor. The liquor contained byproducts of the pretreatment process including lignocellulosic sugars, H_2SO_4, and acetic acid.

Rheologic Measurements

Rheologic measurements were performed at 25°C with the cone-and-plate and the 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 Re_i (Eq. 1). As the impeller's 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 *(9)*.

Results

From the Newtonian calibration fluids measurements, the value for the constant, c, was determined to be 135. Figure 2 shows the typical example of the torque-impeller speed curves in the case of silicone oil. Figure 3 shows the relationship between the impeller constant, c, and the

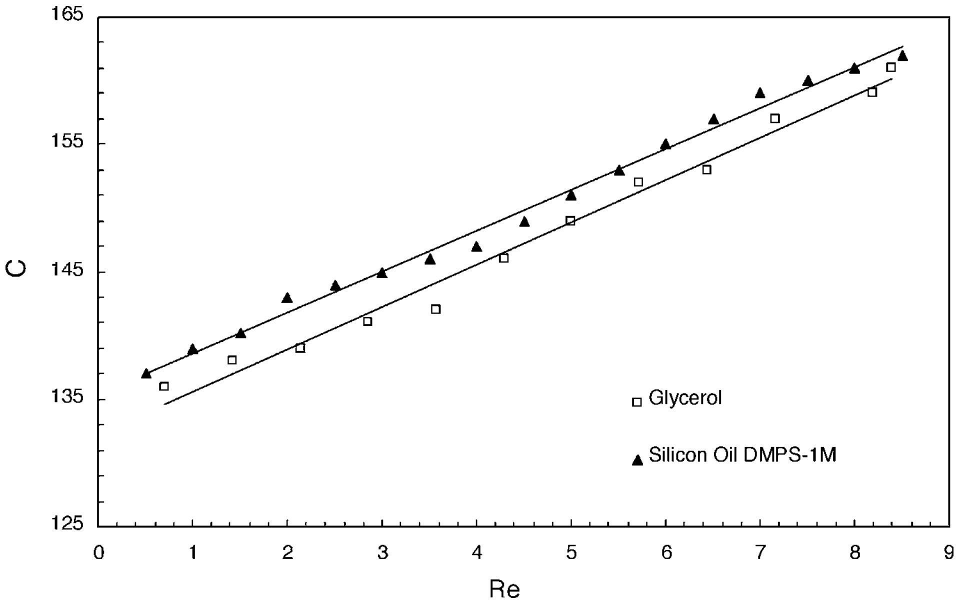

Fig. 3. Relationship between *c* and *Re* for glycerol and silicone oil DMPS-1M using helical impeller.

Re for silicone oil and glycerol. The deviation in the value of *c* between *Re* 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%. Figure 4 compares the helical impeller and cone-and-plate data for the 0.5 and 1.0% xanthan gum solutions.

The average value for *k* determined for each solution is shown in Table 1 along with the power law indices calculated from the cone-and-plate and impeller viscometer data for each fluid. The shear rate constant *k* obtained from the cone-and-plate and helical impellers 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 *(6,11)*.

The results of the rheologic measurements for the corn stover suspensions are presented in Fig. 5. Corn stover suspensions of 5, 10, 20, and 30% were used. The viscosity of the suspension increased as the fiber loading increased, as expected. The power law parameters (the consistency index number, *n*; the power law parameters, K_{pl}) for the various fiber suspensions are presented in Table 2 and may be compared with the results of Dronawat et al. *(11)*, who conducted tests with the Solka-Floc fiber of similar length (215 μm). The parameters are independent of the method of measuring rheologic data and dependent on the fluid.

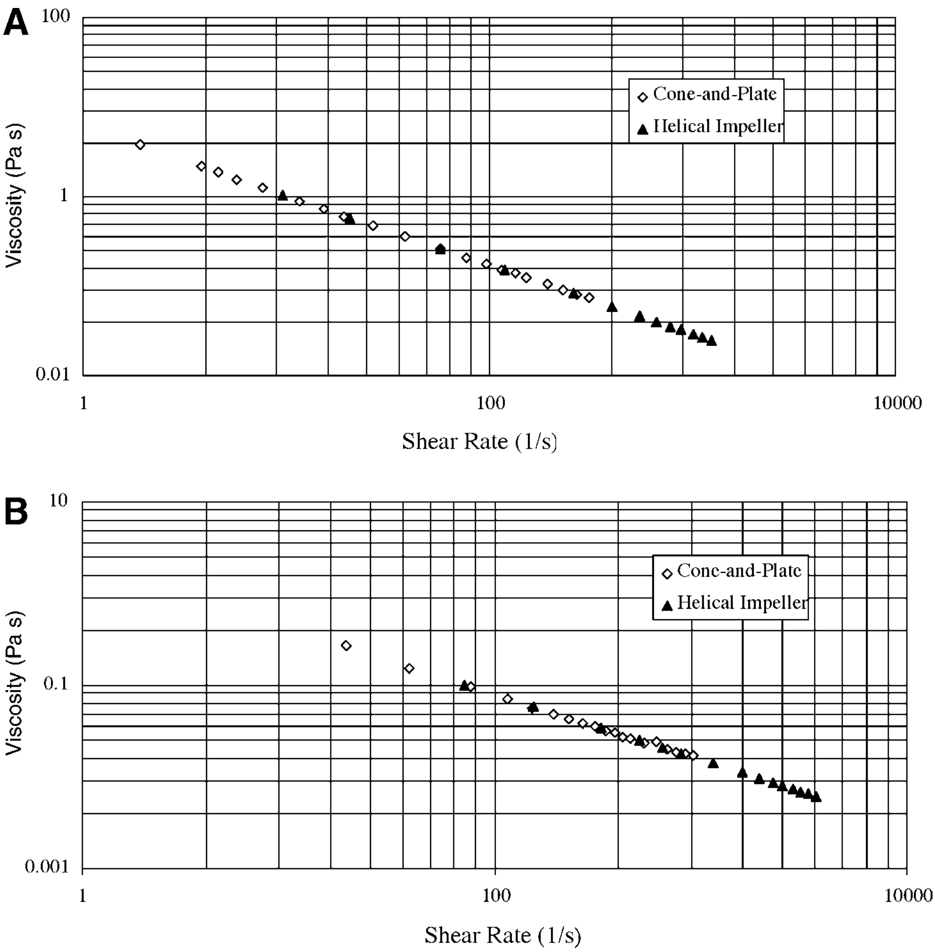

Fig. 4. Shear rate vs viscosity for (**A**) 0.5 % and (**B**) 1.0 % xanthan gum.

Table 1
Values of Shear Rate Constant for Different Fluids and 1000-mL Vessel

		n	
Solution	*k*	Cone-and-plate impeller	Helical impeller
Xanthan Gum			
0.5%	10.8 ± 1.2	0.37	0.39
1.0%	10.1 ± 1.7	0.26	0.23
1.5%	10.8 ± 0.6	0.19	0.19
Guar gum			
0.5%	11.6 ± 1.3	0.45	0.44
1.0%	11.2 ± 0.7	0.31	0.29
1.5%	11.0 ± 1.0	0.19	0.18

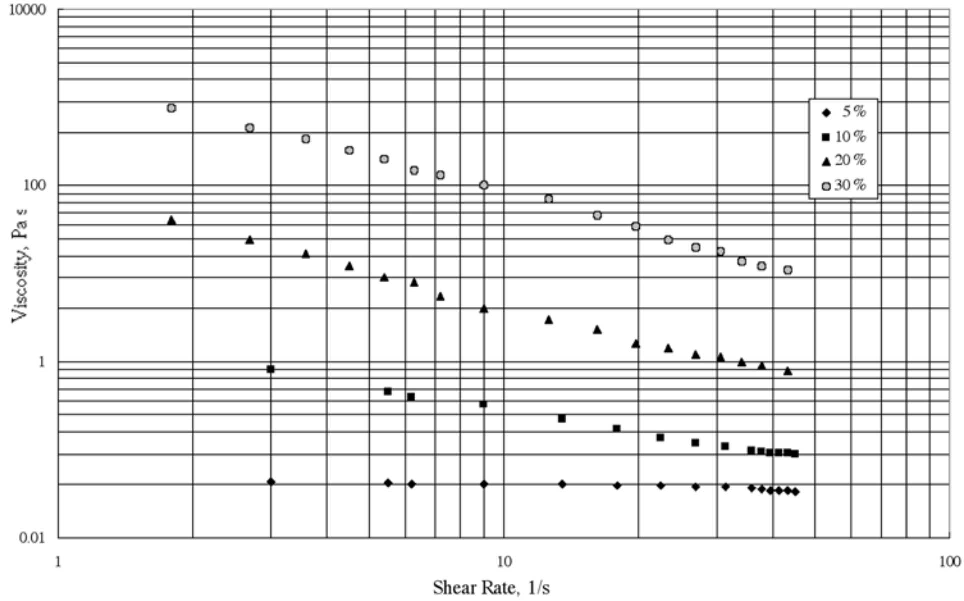

Fig. 5. Rheology of corn stover suspensions.

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. It allows the helical impeller viscometer to be calibrated for homogenous non-Newtonian fluids, which are difficult to analyze by conventional rheologic instruments. Xanthan and guar gum solutions were chosen as non-Newtonian calibration fluids, because their rheologic behavior at low shear rates is similar to that of yield stress fluids. The calibration results for guar and xanthan gum solutions ranging in concentration from 0.5 to 1.5% produced a single value of $k = 10.8$ sufficient to represent all the data.

The power law indices obtained using the helical impeller compare well with the cone-and-plate viscometer results, as can be seen in Tables 1 and 2. The difference in the value of k may be explained by the fact that in the vicinity of the low-shear Newtonian transition, the viscosity is relatively insensitive to the shear rate, which is not desirable for determining k.

Corn Stover Suspensions

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

The power law parameters for the corn stover suspensions could not be located in previous studies. Dronawat et al. *(11)* studied a similar system

Table 2
Power Law Parameters for Non-Newtonian Solutions Used

Solution	K_{pl} (Pa·s)	n	R^2
Helical impeller			
Xanthan gum			
0.5%	2.09	0.29	0.97
1.0%	6.02	0.23	0.98
1.5%	13.56	0.23	0.99
Guar gum			
0.5%	0.78	0.44	0.99
1.0%	4.77	0.29	0.99
1.5%	16.32	0.18	0.98
Corn stover suspension			
5%	0.05	0.91	0.90
10%	1.87	0.08	0.99
20%	71.82	0.06	0.99
30%	1684.50	0.05	0.99
Cone-and-plate			
Xanthan gum			
0.5%	2.07	0.29	0.98
1.0%	6.01	0.22	0.98
1.5%	13.55	0.22	0.99
Guar gum			
0.5%	0.69	0.42	0.99
1.0%	4.68	0.31	0.99
1.5%	17.00	0.18	0.98

using filamentous particles (Solka-Floc with a fiber length of 215 μm in a 0.5% xanthan gum water solution). Comparison of the power-law parameters indicates that the suspensions studied herein were less viscous and less shear thinning than the suspensions Dronawat et al. *(11)* studied. The difference can be attributed to the fact that our study used water rather than a 0.5% xanthan gum solution. In both studies the increase in the consistency index as the power law index increased was moderate.

Conclusions

The parameter c is a linear function of Re. The linear regression analysis performed on the data collected for glycerol and silicone oil yielded regression coefficients ranging from 0.98 to 0.998. Furthermore, the shear rate constant is independent of the rheologic properties of the fluid. The percentage difference between the highest and lowest values of shear rate constant calculated for the xanthan and guar gum was 10% (10.9 ± 1.1). The impeller method can accurately and reliably measure the rheologic properties of filamentous suspensions, based on the results obtained from the corn stover suspension experiments.

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