Madras Agric. J., **2017,** *104 (7-9)*: 279-281; doi: 10.29321/MAJ.2017.000060

Rheology of Different Corncob Biomass Slurries for Hydrodynamic Cavitation Based Biomass Pretreatment Process

[1]T. Kiruthika, [2]D.Ramesh and [3]Sivakumar Uthandi
[1,2]Department of Bioenergy, AEC & RI, TNAU, Coimbatore - 641003
[3]Department of Agricultural Microbiology, TNAU, Coimbatore - 641003

Rheology properties of biomass slurry are considered essential for designing a bioreactor to understand the flow behaviour of materials inside the reactor. The biochemical composition of raw corncob samples used in this study include: 36 % of cellulose, 27.38% of hemicellulose and 17.60 % of lignin. Rheological measurements of corncob biomass slurrires at loadings of 2.50, 3.75 and 5.00 % indicated a non Newtonian behaviour, showing yield stress and shear thinning. Based on the results, it is concluded that, corncob biomass slurry loaded up to 5% could be well suited for hydrodynamic cavitation reactor used for pretreatment process.

Key words: Corncob biomass, Slurry, Rheology, Hydrodynamic cavitaion, Pre-treatment

Rheology plays a vital role in designing cost effective processes such as biomass pretreatment, fermentation and handling of different biomass slurries (Riedlberger and Weuster-Botz, 2012). It is also used to understand the product's structural behavior (Steffe, 1996), which is esstential for designing the materials handling machineries. Rheological behaviour depends on various factors, including chemical composition, particle size and shape, surface effects and / or additives presenent. These factors are generally heterogeneous in biomass suspensions, once particles vary in terms of composition, size and shape (Stickel *et al.*, 2009). The flow characteristics of suspensions can be defined both by the continuous or dispersed phase and even by the influence of one on another (Ferguson and Kemblowski, 1991). Development of pretreatment reactor handled with high biomass loading involves more challanges in design, especially material mixing and handling process (Jørgensen *et al.*, 2007a). Therefore, an understanding of flowbehaviour and their rheology, during the biomass conversion to simple sugars will provide perceptiveness into the processing challenges. Methods to measure various rheological properties of concentrated pretreated corn stover (PCS) have been previously investigated (Pimenova and Hanley, 2003, 2004; Viamajala *et al.,* 2009). The present study has been conducted to evaluate the rheological behaviour of different corncob biomass slurries prepared at various biomass loadings, which may be useful to design a bioreactor for hydrodynamic cavitation based pretreatment process.

Material and Methods

Biomass preparation

The lignocelluosic biomass feedstock selected for this study was corncob biomass, which was dried up to 14 % moisture, followed by size reduction in a sequence shredder, pin mill, and grinder. The powdered biomass was sieved with ASTM 70 sieve and the final size of the biomass particles used for the experiment was < 212 μm.

Chemical characterization and rheological measurements

The cellulose, hemicellulose and lignin contents of the biomass were analysed following the the protocol suggested by National Renewable Energy Laboratory (NREL) (Sluiter *et al*., 2004). The rheological properties of corncob biomass slurry were studied by using the Modular Compact Rheometer MCR 52 (Anton Parr) equipped with spindle ST 24-2D/2V/2V-30. The properties such as viscosity–shear rate and shear stress–shear rate relationship of the biomass slurries were measured at different shear rates from 1 to 100 s^{-1}. The experiments were carried out at 30°C at different biomass loadings *viz*., 2.50, 3.75, 5.00, 6.75, 7.5, 8.75 and 10.00 %. Bingham, Power law, Casson, Ostwald and Herschel-Bulkley rheological models were used to describe viscous flow behaviours of biomass slurries (Pimenova and Hanley, 2003; 2004). Corncob biomass slurries were uniformly mixed before sample testing. The rheological data were obtained from the Rheoplus 32V3.61 software and used for further analyses.

Results and Discussion

Chemical characterization

The cellulose, hemicelluloses and lignin content of corncob samples were found to be 36.00, 27.38 and 17.60 %, respectively. A similar range of values for cellulose (37.4-45 %), hemicellulose (35-40.8 %) and lignin (15-18.8 %) was reported by Sun and Cheng (2002) and Parajo *et al.* (2004) for corncob samples.

Rheological properties of selected biomass

The apparent viscosity and yield stress of the tested corncob slurry samples (2.50, 3.75, 5.00, 6.75,

*Corresponding author's e-mail: rameshd@tnau.ac.in

7.5, 8.75 and 10.00 %) were measured by modular compact rheometer at 30°C. From the experimental data, two plots were drawn for shear stress (Pa) versus shear rate (s^{-1}) and viscosity (Pa.s) versus shear rate (s^{-1}). The following rheological models were employed to analyse the experimental data.

Herschel-Bulkley model	:	$\tau = \tau_y + K\gamma^n$ ---------- (1)
Bingham model	:	$\tau = \tau_y + K\gamma$ --------- (2
Casson model	:	$\tau^{0.5} = (\tau_y)0^{.5} + n\,(\gamma^n)^{0.5}$--(3)
Ostwald model	:	$\tau = K\gamma^n$ --------- (4)
Newton model	:	$\tau = \mu\gamma^n$ ---------- (5)

Casson model was found to be the best fit for the shear stress versus shear rate of tested biomass slurries and it showed a good representation of the experimental data as compared to the other four models. The R^2 value is a measure of the goodness of fit and it ranged from 0.58 to 0.98, 0.51 to 0.89, 0.45 to 0.92 and 0.04 to 0.75 for Casson, Ostwald, Herschel - Bulkley and Bingham models, respectively for biomass loading from 2.5 to 5 % (Table 1). If the biomass loading exceeds 5 %, R2 values were not showing the goodness of fit. Hence, more than 5 % biomass loading was not considered for further discussion. Hence, the biomass loading of 2.50, 3.75 and 5.00 % were taken for optimizing the biomass loading rate in the catalytic HCR.

Flow behaviourof the corncob biomass slurries was mainly influenced by the yield stress. Yield stress provides the necessary initial energy to induce the flow of biomass slurries, at high solid concentration. The biomass particles were found to be highly disordered and misaligned, thereby, increasing the residual stress. The breakdown of a three dimensional structure along with the increase of shear rate caused the release of interstitial water, thereby reducing the apparent viscosity, resulting in shear thinning behaviour (Sato, 1995; Seka and Verstraete, 2003).

For any non Newtonian fluid, the relationship between shear stress and shear rate is not a constant. The viscosity of this kind of fluids depends on the applied shear force and time. Shear-thinning behaviour was observed for all the tested biomass slurries. It clearly showed that a decrease in viscosity of biomass slurry was observed with respect to increase in shear rate. The corncob biomass slurry at different time intervals followed the non Newtonian fluid behaviour. The main cause for this kind of flow behaviour may be due to breakdown of structural units of tested materials and the hydrodynamic forces generated by shear action (Rao, 2007). The Casson model has been used to model shear-thinning behaviour in a diverse range of materials including blood, printing ink, food products, mineral, polymer suspensions and composites (Nguyen and Boger, 1992), also biomass slurries (Pimenova and Hanley, 2004).

Table. 1. Comparison of rheological model tested for different biomass loading rates

Biomass loading%	Herschel-Bulkley model				Bingham model			Ostwald model		Casson model			Newton model
	τ (Pa)	N	R^2	s(n-1)	τ (Pa)	s(n-1)	R^2	R^2	s(n-1)	τ (Pa)	R^2	s(n-1)	s(n-1)
2.50	836.22	0.01	0.45	7.52	12.94	9.96	0.04	0.89	3.38	37.98	0.58	6.57	15.10
3.75	8.77	1.93	0.99	--	10.13	--	0.99	0.99	--	16.13	0.99	--	7.50
5.00	2311	0.01	0.92	31.77	279.32	55.76	0.75	0.51	78.27	1806.6	0.98	14.09	166.99
6.25	23.50	0.59	--	91.17	20.36	91.46	--	0.17	82.87	28.46	0.01	90.71	95.06
7.50	19.90	1.06	0.01	43.19	20.11	43.16	0.01	0.24	37.94	26.88	0.04	42.55	47.16
8.75	21.63	0.97	0.04	30.37	21.50	30.39	0.04	0.31	25.73	29.38	0.08	29.68	35.11
10.00	479.76	0.01	0.22	15.61	22.37	16.88	0.09	0.47	12.89	30.48	0.17	16.08	23.00

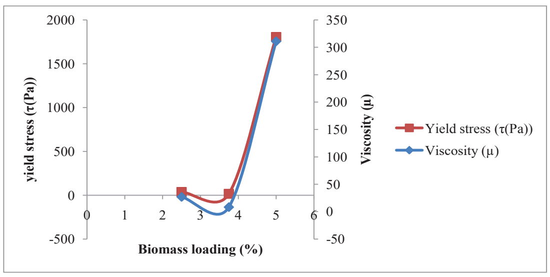

Fig. 1. Viscosity and yield stress as function of biomass loading

The negative value of the plotted curves (Fig. 1) implies that these slurries exhibit pseudo-plastic or shear-thinning behaviour in the range of shear rates tested for the biomass slurries. Exact mechanism leading to pseudo-plasticity in biomass slurries was not known (Pimenova and Hanley, 2003, 2004). It was clearly seen that viscosity and yield stress, increased with increase in biomass solid loading (Fig. 1). A similar result has been reported for corn stover slurries (Pimenova and Hanley, 2003, 2004). A decrease at 3.75 % as shown in Fig.1 indicates that the biomass loading might have been influenced by particle size, shape, size distribution and aspect ratios (Chang and Powell, 2002; Goto *et al.,* 1986; Goudoulas *et al.,* 2003; Liu and Masliyah, 1996; Roh *et al.,* 1995; Stickel and Powell, 2005; Vladu *et al.,* 2006). This shear thinning behavior was also observed in different kind of suspensions such as fruit pulps like tomato (Sharma *et al.,* 1996), mango (Bhattacharya, 1999), slurries of limestone (He *et al.,* 2006), nickel (Bobicki *et al.,* 2014) and biomass of corn stover (Viamajala *et al.,* 2009).

Conclusion

Rheological study concluded that Casson model was the best fit for corncob slurries with biomass loading of 2.50, 3.75 and 5.00 % and they exhibited pseudoplastic or shear-thinning behaviour. Results also showed that, biomass loadings of up to 5 % of corncob slurries could be used to design bioreactor for hydrodynamic cavitation based pretreatment process.

References

Bhattacharya, S. 1999. Yield stress and time-dependent rheological properties of mango pulp, *Journal of Food Science.,* **64:**1029–1033.

Bobicki, E.R.,Q. Liu and Z. Xu. 2014. Effect ofmicrowave pre-treatment on ultramafic nickel oreslurry rheology, *Miner. Eng.,* **61:**97–104.

Chang, C. and R.L. Powell. 2002. Hydrodynamic transport properties of concentrated suspensions. *AIChE Journal,* **48:**2475–2480.

Ferguson, J. and Z. Kemblowski. 1991. Applied Fluid Rheology, Elsevier, New York.

Goto, S.,H. Nagazono and H. Kato. 1986. The flow behavior of fiber suspensions in Newtonian fluids and polymer solutions. I. Mechanical properties. *Rheologica Acta,* **25:**119–129.

Goudoulas, T.B., E.G.Kastrinakis and S.G. Nychas. 2003. Rheological aspects of dense lignite-water suspensions; time dependence, preshear and solids loading effects. *Rheologica Acta,* **42:**73–85.

He, M.,Y. Wang and E. Forssberg. 2006. Parameter studies on the rheology of limestone slurries,*Int. J. Miner. Process*., **78:**63–77.

Jorgensen, H., J.B. Kristensen and C.Felby. 2007a. Enzymatic conversion of lignocellulose into fermentable sugars: Challenges and opportunities. *Biofuels Bioproducts and Biorefineries.,* **1(2):** 119–134.

Liu, S. and J.H. Masliyah. 1996. Rheology of suspensions. In: Schramm, L. (Ed.), Suspensions: Fundamentals and Applications in the Petroleum Industry. *Advances in Chemistry Series,* **251:**107–176.

Nguyen, Q.D. and D.V. Boger. 1992. Measuring the flow properties of yield stress fluids. *Annual Review of Fluid Mechanics,* **24:**47–88.

Parajo, J.C., G.Garrote Cruz and H. Dominguez. 2004. Production of xylooligosaccharides by auto hydrolysis of lignocellulosic materials. *Trends in Food Science and Technology,* **15:**115–120.

Pimenova, N.V. and T.R. Hanley. 2003. Measurement of rheological properties of corn stover suspensions. *Applied Biochemistry and Biotechnology.,* **106:**383–392.

Pimenova, N.V. and T.R. Hanley. 2004. Effect of corn stover concentration on rheological characteristics. *Applied Biochemistry and Biotechnology.,* **114:**347–360.

Rao, M.A. 2007.Rheology of liquid foods - a review. *Journal of Texture Studies,* **8:** 135–168

Riedlberger, P. and D. Weuster-Botz. 2012. New miniature stirred-tank bioreactors for parallel study of enzymatic biomass hydrolysis. *Bioresoure Technology.,* **106:**138–146.

Roh, N.S., D.H. Shin, D.C. Kimand and J.D. Kim. 1995. Rheological behavior of coal water mixtures. 1. Effects of coal type, loading and particle size. *Fuel,* **74:**1220–1225.

Sato, T. 1995. Rheology of suspensions, *Journal of Coatings Technology.,* **67:**69–79.

Seka, M.A. and W. Verstraete. 2003. Test for assessing shear sensitivity of activated sludgeflocs: a feasibility study. *Water Resources.,* **37:**3327–3334.

Sharma, S.K., M. LeMaguer, A. Liptay and V. Poysa. 1996. Effect of composition on the rheologicalproperties of tomato thin pulp. *Food Res. Int.*, **29:** 175–179.

Sluiter, A., B. Hames, R.Ruiz, C. Scarlata, J. Sluiterand and D. Templeton. 2004. Determination of structural carbohydrates and lignin in biomass**.** Golden (CO): National Renewable Energy Laboratory.

Steffe, J.F. 1996. Rheological Methods in Food Process Engineering, second ed. Freeman Press, East Lansing.

Stickel, J.J. and R.L. Powell. 2005. Fluid mechanics and rheology of dense suspensions. Annual *Reviews in Fluid Mechanics*, **37:**129–149.

Stickel, J.J., J.S.Knutsen, M.W.Liberatore,W.Luu, D.W. Bousfield, D.J.Klingenberg, C.T.Scott, T.W. Root, M.R. Ehrhardt and T.O. Monz.2009. Rheology measure ments of a bio- mass slurry: an inter-laboratory study, *Rheolodica Acta.,* **48:**1005–1015.

Sun, Y. and J. Cheng. 2002. Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology,* **83:**1-11.

Viamajala, S., J.D. McMillan, D.J.Schell and R.T. Elander. 2009. Rheology of corn stover slurries at high solids concentrations - Effects of saccharification and particle size. *BioresoureTechnolonogy.,* **100(2):** 925–934.

Vladu, C.M., C.Hall and G.C. Maitland. 2006. Flow properties of freshly prepared ettringite suspensions in water at 25°C. *Journal of Colloid and Interface Science*., **294:**466–472.

Received : June 10, 2017; Revised : July 02, 2017 Accepted : August 16, 2017